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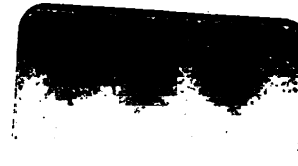
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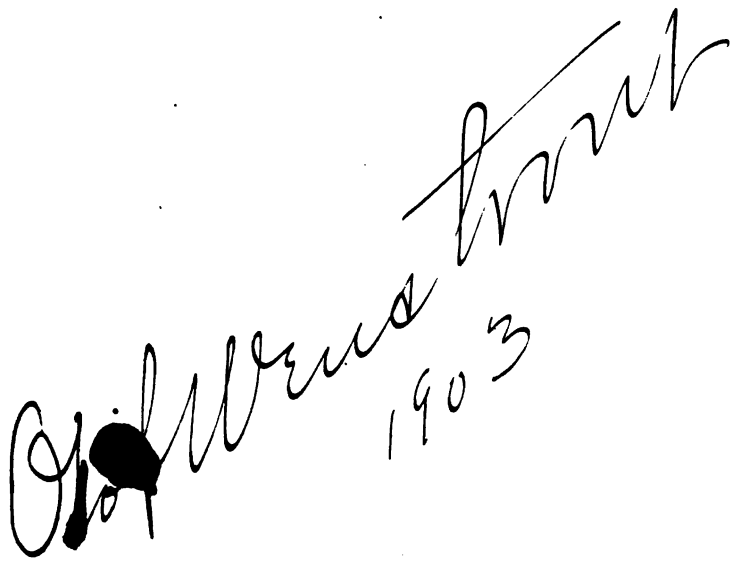
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HANDBOOK OF METALLURGY



HANDBOOK

OF

METALLURGY

BY

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VOL. I

COPPER—LEAD—SILVER—GOLD

London

MACMILLAN AND CO., LIMITED

NEW YORK: THE MACMILLAN COMPANY

1898

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RICHARD CLAY AND SONS, LIMITED,
LONDON AND BUNGAY.

PREFACE

It is a curious fact that there does not exist in the English language a single complete treatise on Metallurgy. There are a number of smaller text-books, mainly adapted to the use of students, which cover the entire field, but make no pretence of describing it with any thoroughness of detail; and there are a number of very admirable works dedicated to the metallurgy of individual metals. Had my respected teacher, the late Dr. John Percy, ever carried out his magnificent idea of a comprehensive series of volumes on this subject, the ideal of an exhaustive work on Metallurgy would have been produced, although its bulk would have attained the formidable dimensions of a small library in itself—an advantage perhaps to the specialist, but a less commendable feature for those who have to deal with general Metallurgy.

Such being the position of our literature of this subject, I venture to think that I am rendering the English metallurgist a distinct service in submitting to him a translation of the most recent and most exhaustive work on the subject in any language, from the pen of that eminent metallurgical authority, Dr. C. Schnabel, of Clausthal. The object of his work has been to give a complete account of the metallurgical treatment of every one of the metals ordinarily employed, together with all the recent improvements in the art, whilst at the same time pointing out the scientific principles underlying

each process, and illustrating each by examples drawn from actual practice in various parts of the world. Our author is especially fitted for this task, having had many years' practical experience as a metallurgist both in his own country and abroad, whilst he has been for nine years professor of this subject at the Royal Mining Academy of Clausthal, and has had especially favourable opportunities for studying the metallurgical methods employed not only in Germany, but also in the other countries of Europe, in America, Asia, and Australia, in the course of his extensive travels.

He has at the same time availed himself fully of all contemporary Metallurgical literature, and especially of the works of three well-known American writers, namely Egleston, Peters and Hofman. His illustrations have been drawn partly from material collected by himself, partly from the authors named, and from his own previous work and that of Balling on the same subject.

The work is divided into two volumes. The first embraces the metallurgy of copper, lead, silver and gold, which were grouped together, firstly because they so often occur together in the same mineral deposits that they are often necessarily extracted side by side from their ores; and, secondly, because their treatment has been so profoundly modified by recent improvements that more space is required for the description of the methods employed in their extraction than for that of all the other metals put together. The remaining metals are treated of in Volume II., the most important among them being zinc, nickel and mercury.

As regards my own task as translator, my chief object has been to present a faithful interpretation of the original, and I have therefore subordinated the style of the work to the all-important consideration of accuracy. With the full consent and authorization of Dr. Schnabel, I have in some places introduced brief notices of any new processes or improvements on old ones, that have been brought out since the German original was produced. These are naturally

most frequent in the first volume, which was published in 1894, or more than two years before the second volume, and are largely confined to gold, the metallurgy of which has made such rapid advances in recent years. I have also been at pains to correct as fully as possible all typographical errors in the original. The opinions expressed are, however, throughout the author's own, my responsibility being confined to their faithful rendering into English.

I have been assisted in this task by Mr. Saville Shaw, M.Sc., of the Durham College of Science, and Mr. John McKillop, late of Pulo Brani, Singapore. The former has translated the sections on lead and silver, the latter the second half of Volume II. from the section on tin onwards; and he has also contributed a brief account of his own method of tin smelting at Pulo Brani. I am greatly indebted to these gentlemen for the zeal and knowledge which they have brought to bear on their work, but think it only right to add that I have repeatedly revised their translations, and am fully prepared to take upon myself the sole responsibility for any errors that may be found, whether in this part or in the remainder of the translation.

HENRY LOUIS.

THE DURHAM COLLEGE OF SCIENCE,
NEWCASTLE-UPON-TYNE. 1898.

CONTENTS

COPPER

PAGE

Physical Properties 1
Chemical Properties 6
Chemical Reactions of the Compounds of Copper that are of importance in its Extraction 7
Cuprous Oxide 7
Cupric Oxide 8
Silicates of Copper 9
Sulphide of Copper 9
Cupric Sulphate 12
Cuprous Chloride 12
Cupric Chloride 12
Ores of Copper 13
The Extraction of Copper 16
Dry Methods of Copper Smelting 17
Extraction of Copper from its Sulphur Compounds 17
Blast Furnace Smelting, 18; Reverberatory Smelting, 19; Converter Process, 21.
Comparison of the Various Processes for Producing Coarse Copper in the Dry Way 22
The German Process of Copper Extraction 24
Calcination of the Ores 25
The Operation of Roasting 26
Heap Roasting 28
Normal Heap Roasting 29
Kernel Roasting 34
Heap Roasting of Fines 37
Removal of Bitumen from Copper Ores by Heap Roasting 38
Roasting in Stalls 38
Roasting in Shaft Furnaces 44
Calcination of Lump Ores in Shaft Furnaces 45
Pyrites Burners 45
Kilns 49
The Roasting of Ore-Fines in Shaft Furnaces 52
Gerstenhöfer Furnace, 52; Hasenclever and Helbig Furnace, 56; Ollivier and Perret Furnace, 57; Malétra Furnace, 58; Spence Furnace, 62; MacDougall Furnace, 65.

PAGE
Calcination in Reverberatory Furnaces 67
Calcination in Fixed Hearths worked by Hand 68
Long-bedded Calciners (*Fortschaufelungsöfen*) 68
Calcination in Fixed Reverberatory Furnaces by the aid of Machinery . 72
O'Harra Furnace, 72; Pearce's Turret Furnace, 75; Brown Horseshoe Furnace, 76; Parkes's Furnace, 78.
Calcination in Reverberatory Furnaces with Movable Beds 80
Calcination in Reverberatory Furnaces with Movable Working Chambers 80
Brückner Furnace, 80; White Calciner, 81; Hocking-Oxland Furnace, 82.
Calcination in Muffle Furnaces 83
Hasenclever Furnace, 83; Douglas Furnace, 85.
Smelting the Calcined Ore for Matte in Shaft Furnaces 86
Spurröfen, Tiegelöfen, Sumpföfen, 93.
Older Furnaces 96
Krummofen, 96; Sulu Furnace, 97.
Modern Furnaces 98
Furnaces of Circular Cross-Section 98
Oker Furnace, 98; Mansfeld Furnace, 100; Water-jacket Furnace, 101.
Furnaces Rectangular in Cross-Section 104
Orford Furnace, 104; Henrich Furnace, 105.
Furnaces Oval in Cross-Section 107
Skinder Furnace, 107; Herreshof Furnace, 107.
The Process of Ore Smelting 109
Products of the Fusion 110
Calcination of the Matte 112
Dead-roasting of the Matte in Heaps, 113; Dead-roasting of Matte in Stalls, 115; Calcination in Shaft Furnaces, 115; Calcination in Reverberatory Furnaces, 116; Calcination in Muffle Furnaces, 116.
Smelting the Roasted Matte for Coarse Copper 117
The German Process of Copper Extraction Combined with the Concentration of Matte 120
Examples of the German Process of Copper Smelting 122
Brixlegg, 122; Kedabeg, 123; Atvidaberg, 123; Agordo, 124; Stefanshütte, 124; Mühlbach, 124.
The English Process of Copper Smelting 125
The Simple English Process 126
Calcining the Ores 126
Smelting the Calcined Ore for Coarse Metal in Reverberatory Furnaces 129
Calcination of Coarse Metal 139
Smelting the Calcined Coarse Metal for White Metal 140
Smelting the White Metal in Reverberatory Furnaces for Coarse Copper 143
Smelting White Metal for Coarse Copper after previous Calcination . 143
Smelting White Metal for Coarse Copper without Calcination (Roasting) 144

PAGE

The English Process with repeated Concentration Operations (Welsh Process) 147
Treatment of Copper Bottoms 151
Examples of the English Process of Copper Smelting 152
The Anglo-German Process of Copper Smelting 153
Mansfeld, 154 ; Oker, 155.
Copper Extraction by means of the Converter, or the Copper Bessemer Process 158
Manhés Converter, 160 ; Stalmann Converter, 162.
Pyritic Smelting 166
The Extraction of Copper from Oxides and Salts of Copper, and from Ores that contain Native Copper 167
Purification of Coarse Copper (in the Dry Way) 169
Purification of Copper by Separate Refining and Toughening, 171 ; Production of Dry Copper, 171 ; Production of Tough Pitch Copper, 180.
The Purification of Copper by Combined Refining and Toughening in the Refining Hearth 181
Refining of Copper (English Process) 181
Examples of Copper Refining 195
Extraction of Copper by Wet Methods 198
The Extraction of Copper from Ores that contain it as Oxide or Carbonate 199
The Solution of the Copper 199
Lixiviation with Sulphuric Acid, 199 ; with Hydrochloric Acid, 200 ; with Solutions containing Ferrous Chloride, 201 ; with other Solvents, 204.
Precipitation of the Copper 205
The Extraction of Copper from Ores that contain it in the form of Sulphates 208
The Extraction of Copper from Ores that contain it as Sulphide . . 210
Transformation of the Copper into a form suitable for Solution . . 210
The Transformation of Sulphide of Copper into Sulphate, 210 ; by Weathering, 211 ; by slow Calcination, 211 ; by Calcination with Sulphate of Iron or other readily Decomposable Sulphates, 213 ; by Heating with Nitrate of Iron, 215 ; by the aid of Ferric Sulphate, 215.
The Transformation of Sulphide of Copper into Oxide 216
The Conversion of Sulphide of Copper into Chloride 216
Formation of Chloride of Copper in the Wet Way, 217 ; Production of Chloride of Copper in the Dry Way, 220.
Dissolving the Copper out of the Ores 236
Solution of Copper as Sulphate, 236 ; Solution of Oxide of Copper, 236 ; Solution of Chloride of Copper, 237.
The Precipitation of Copper from its Solutions 240
From Cupric Sulphate, 240 ; from Solutions of Chloride of Copper, 241.
Conversion of Copper Precipitate (Cement Copper) into Merchantable Copper 246
Extraction of Copper in the Wet Way from Furnace Products . . 248

PAGE
The Extraction of Copper by Electro-Metallurgical Methods . . . 248
The Extraction of Copper from Ores 249
The Siemens and Halske Process, 249 ; Höpfner's Process, 256.
Extraction of Copper from Mattes 257
Marchese Process, 257.
Extraction of Copper from its Alloys 260

LEAD

Physical Properties 275
Chemical Properties 276
Chemical Reactions of Lead Compounds that are of importance in the Production of the Metal 276
Lead Monoxide 276
Lead Sulphide 277
Lead Sulphate 280
Lead Carbonate 280
Lead Silicate 280
Lead Antimoniate 281
Lead Chloride 281
Lead Alloys 281
Ores of Lead 281
The Production of Metallic Lead 283
Extraction of Lead from its Ores 284
The Extraction of Lead from Galena 284
The Air-Reduction Process 286
The Air-Reduction Process in Reverberatory Furnaces 288
The Carinthian Process 290
The English Process 296
The Tarnowitz Process 303
The Bleiberg Process at Mons 306
The French or Brittany Process 308
Smelting by the Air-Reduction Process in Hearths 310
The Roasting and Reduction Process 319
The Roasting of the Ores 322
The Preparatory Roasting of the Ore 323
Roasting in Heaps, 324 ; in Stalls, 328 ; in Shaft Furnaces, 328 ; in Reverberatory Furnaces, 329 ; in Reverberatory Furnaces with Movable Hearths, 338.
The Smelting of the Roasted Ores in Shaft Furnaces 339
Smelting Furnaces 348
Draught Furnaces 348
Blast Furnaces 351
Construction of the Furnace 355
The Arents Syphon Tap, 356.
Older Forms of Furnace 362
Recent Furnaces 368
Pilz Furnace, 368 ; Raschette Furnace, 370.
The Smelting Process 377
Products obtained by Smelting in the Blast Furnace 381
Treatment of the Lead Matte 383

PAGE
Examples of the Roasting and Reduction Process 385
Smelting at the Sophien Works, near Langelsheim, and the Julius Works, near Goslar, 385 ; at Freiberg, 386 ; at Mechernich, 390 ; at Altenau in the Upper Harz, 390 ; at Przibram in Bohemia, 391 ; at Denver, Colorado, 392 ; in Spain, 394.
The Iron-Reduction Process 394
The Iron-Reduction Process in the Upper Harz 397
The Smelting of Lead Matte 404
The Combined Roasting and Reduction and Iron-Reduction Process . 409
The Combination of the Iron-Reduction Process with the Smelting of Oxidised Ores 412
The Smelting of Lead Carbonate 413
The Smelting of Lead Sulphate 416
The Smelting of Plumbiferous Metallurgical Products 418
Residues from the Air-Reduction Process 419
The Slag Hearth, 419.
Lead Mattes and Slags 420
Furnace Accretions, Dross, Furnace Residues and Flue Dust . 421
Smelting of Bye-products Obtained in the Cupellation Process . . . 422
The Refining of Lead 430
Refining in Fore-hearths, 433 ; in Pots, 434 ; in Reverberatory Furnaces, 443.
The Casting of Refined Lead 453

SILVER

Physical Properties 456
Chemical Properties 457
The Chief Chemical Reactions of Silver Compounds that are of importance in its Extraction 457
Oxides of Silver 457
Silver Sulphide 458
Silver Chloride 460
Compounds of Silver with Arsenic, Antimony and Sulphur 462
Silver Alloys 463
The Ores of Silver 465
Argentiferous Products obtained in Smelting 468
The Extraction of Silver from its Ores 468
The Extraction of Silver by Dry Methods 470
The Production of Work-lead 471
The Production of Work-lead from Ores 471
From Rich Ores, 472 ; Leading in Crucibles, 473 ; in Lead Baths, 473.
The Production of Work-lead from Medium Silver Ores 474
The Production of Work-lead from Poor Silver Ores 480
The Production of Work-lead from Metallurgical Bye-products . . 485
The Leading of Mattes, 485 ; in a Bath of Molten Lead, 486 ; Smelting with Materials containing Lead, 489
Desilverising Mattes by means of Lead and Copper conjointly . . . 495
Production of Work-lead from Speiss 495
The Desilverisation of Alloys by means of Lead 496

PAGE

The Liquation Process for Desilverising Copper-Silver Alloys . . . 497
The Leading of Argentiferous Copper, 497 ; the Liquation Process, 498 ; the Drying Process, 500.
The Production of Work-lead from other Metallurgical Products . . . 502
The Concentration of the Silver in Work-lead 502
The Pattinson Process 503
The Hand-Pattinsonising Process 505
The Tapping Process or the Mechanical Pattinsonising and the Rozan Process 511
The Mechanical Pattinson Process, 512 ; the Rozan Process, 514.
Desilverising by means of Zinc 519
The Production of the Silver-Lead-Zinc Alloy from Argentiferous Lead, 522 ; the Desilverising Process, 528.
Liquation of the Zinc Scums 533
Treatment of the Desilverised Lead 538
The Production of Rich Lead from the Zinc Alloy 539
The Distillation of the Zinc Scums, 540 ; Smelting Rich Scum with Ferruginous Slags in the Blast Furnace, 548 ; Cupellation of the Rich Scums, 549 ; Melting Zinc Scums with Alkaline Chlorides, 549 ; the Oxidation of the Zinc by Steam, 550 ; Lixiviation of the Oxides Produced in Dezincising, 552 ; the Extraction of Zinc by means of Ammonium Carbonate, 553 ; by means of Sulphuric Acid, 560 ; the Working up of the Dezincised Oxide, 560.
The Combined Pattinson and Zinc Desilverising Processes 561
Silver and Lead Losses in the Zinc Process, 561.
The Production of a Zinc-Silver Alloy from Work-lead 561
The Cupellation of Argentiferous Lead 566
Cupellation in the German Furnace 568
The Process, 577.
Cupellation without additions of Lead 583
Cupellation with additions of Lead during the Process 585
Cupellation in the English Furnace 586
The Refining of *Blicksilver* 596
Refining of, in the Reverberatory Furnace, 596 ; in Crucibles, 599.
The Extraction of Silver by a Combination of Dry and Wet Processes. . 601
By Conversion of the Silver into a Silver-Lead Alloy, 601.
Processes in which the Silver is not Dissolved 602
The Extraction of Silver from Argentiferous Black Copper by means of Sulphuric Acid, 603 ; from Argentiferous Copper Matte by means of Sulphuric Acid, 608.
Processes in which the Silver is Dissolved 610
The Extraction of Silver by the Amalgamation Process 611
The Production of the Amalgam 611
Amalgamation with Mercury alone 614
Amalgamation in Presence of Reagents, but without previous Chloridising Roasting 617
The Cazo Process, 618 ; Kröhnke Process, 620 ; Patio Process, 625 ; the Crushing of the Ores, 627 ; Amalgamation of the Ground Ore in the *Patio*, 631 ; the Chemical Reactions of the *Torta*, 637 ; the Separation of the Amalgam from the Amalgamated Ore, 642 ; the Treatment of the Silver Amalgam, 646.

The Washoe Process of Pan Amalgamation 647
The Crushing of the Ores, 649; the Treatment of the Powdered Ore in the Pans, 654; the Separation of the Amalgam from the Amalgamated Ores, 663; the Treatment of the Amalgam, 665; the Treatment of the Ores after Amalgamation, 670.
Modifications of the Washoe Process 673
The Combination Process, 674; the Boss Process, 674.
Amalgamation with Reagents, preceded by a Chloridising Roasting . 677
The Drying and Crushing of the Ores 677
The Chloridising Roasting of the Ores 682
Barrel Amalgamation Process, 688; Amalgamation of Copper Mattes, 692; of Blister Copper, 693; of Speiss, 694.
Pan Amalgamation (Reese River Process) 696
Tina Amalgamation 700
Amalgamation with a Soluble Salt of Mercury 702
The Recovery of Silver from Silver Amalgam 703
The Production of Silver by Precipitation from Aqueous Solutions . . 707
Processes in which Silver is obtained in Solution as Chloride . . . 707
The Augustin Process 708
The Patera Process 718
The Extraction of Soluble Compounds of Base Metals by means of Water, 723; the Precipitation of the Silver from the Thiosulphate Liquors, 730; the Treatment of the Precipitated Silver Sulphide, 732.
The Kiss Process 732
The Russell Process 733
The Production of Silver from Copper Ores which have undergone a Chloridising Roasting 739
The Ziervogel Process 740
The Extraction of Silver by Electro-Metallurgical Processes 749

GOLD

Physical Properties 752
The Chemical Properties of Gold and its Compounds, that are of importance in its Extraction 753
Gold Ores 756
Native Gold 756
Compounds of Gold with Tellurium 758
Auriferous Metallurgical Products 758
The Extraction of Gold 758
I. Extraction of Gold by Washing 760
II. Extraction of Gold in the Dry Way 763
III. Extraction of Gold by combined Wet and Dry Methods 764
A. Extraction of Gold in the form of a Gold-Mercury Alloy . . . 764
Amalgamation without previous Crushing of the Gold-Bearing Material 765
a. Without previous Concentration 765
b. With previous Concentration 771
Amalgamation of Artificially Crushed Gold-Bearing Material . . 771

PAGE
Amalgamation partly during, partly after Crushing 772
Arrastra-Amalgamation 772
Amalgamation in Mills (Huntington) 773
Amalgamation in Stamp Mills 777
Amalgamation after previous Crushing 789
Amalgamation in Mortars 789
Amalgamation in Rotating Barrels 790
Amalgamation in Hungarian Mills 790
Amalgamation in Pans 795
Amalgamation with the help of Amalgamated Plates 797
Amalgamation in so-called Amalgamators 798
The Designolle Process of Amalgamation 802
The Treatment of Gold Amalgam 802
B. The Extraction of Gold by means of Aqueous Solutions . . . 803
The Plattner Process 804
Calcination of the Ores 806
Chlorination of Gold and Leaching out the Chloride of Gold . 810
Chlorination without Agitation of the Ore 810
a. When Chlorine is Generated outside the Chlorinating Vessel . 810
b. When Chlorine is Generated inside the Chlorination Vat . . 815
Chlorination with Agitation of the Ore 815
Precipitation of Gold from the Solution of its Chloride 819
Extraction of Gold by means of Bromine 827
Treatment of Telluride Gold Ores 827
The MacArthur-Forrest Process 828
I. Solution of the Gold 829
II. Precipitation of the Gold 834
III. Treatment of the Precipitated Gold 837
Other Methods of Precipitation 838
Direct Cyanidation 839
General Remarks 840
C. The Extraction of Gold by the Formation of Alloys from which the Gold is obtained by Parting 841
IV. The Electro-Metallurgical Extraction of Gold 841
Parting 842
A. Parting in the Dry Way 842
Parting by Sulphide of Antimony, or by *guss und fluss*, 843 ; by means of Sulphur and Litharge, 844 ; by Sulphur alone, 845 ; by means of salt or "Cementation," 846 ; by Chlorine Gas or the Miller Process, 847.
B. Parting of Gold by Wet Methods 850
Parting by Nitric Acid 851
Parting by Sulphuric Acid or Refining 853
1. The Preparation for an Alloy suitable for Parting, and its Granulation, 855 ; 2. Solution of the Silver in the Alloy by means of Sulphuric Acid, 858 ; 3. Treatment of the Residue for Gold, 862 ; 4. Recovery of Silver from the Silver Sulphate Solution, 866.
C. Parting of Gold by the Electrolytic Method 873

METALLURGY

COPPER

Physical Properties [1]

Copper is distinguished from all other metals by a peculiar red colour, which is pinkish or yellowish on the fresh fracture of the pure metal, but inclines to purple in the case of copper containing cuprous oxide.

The fracture of cast copper is hackly-granular; in forged or rolled copper it is fibrous, and shows a pale red silky lustre.

Copper crystallises in the cubic system. Its specific gravity, according to Marchand and Scheerer, is 8·940 for pure crystalline copper, 8·914 for electro-deposited copper, 8·921 for cast copper, and 8·952 for rolled and hammered copper. According to Hampe,[2] the specific gravity of pure and perfectly compact copper at 0° C. in vacuo is 8·945, water at 4° C. being taken as unity. Ordinary commercial copper is more or less porous, and its specific gravity varies between 8·2 and 8·5 according to the same authority.

Copper possesses great hardness and tenacity, and is at the same time so extensible that it can be beaten and drawn into the thinnest leaf and wire. By hammering and rolling at ordinary temperatures it becomes harder, but regains its malleability when heated to the melting point of tin.

Its conductivity for heat is 898, gold being taken at 1000. Its electric conductivity is 93·08, silver being taken at 100. The weldability of copper, which is exhibited only at bright redness, is extremely feeble.

The melting-point of copper has not been determined with

[1] See the classical investigations of Hampe, *Zeitsch. f. Berg. Hütt. u. Sal. Wesen.* 1873, 21, 218; 1874, 22, 93; 1876, 24–6. *Chemiker-Zeitung*, 1892, 16, No. 42.

[1] *Zeitsch. f. Berg. Hütt. u. Sal. Wesen.* 1873, 21, 218.

sufficient certainty; it lies between 1000° and 1200° C., and, according to Violle, is about 1054°. Molten copper is very fluid, and has a sea-green colour. Below its melting-point it becomes so brittle that it can be broken into pieces and pounded to powder.

At more elevated temperatures (before the oxyhydrogen blowpipe, and according to the investigations of Sir C. W. Siemens in the electric arc) it is volatile, and burns in the air with a green flame.

When cast in moulds, copper has the property of rising and becoming porous. Sound castings can only be obtained by means of special precautions, such as pouring at the lowest possible temperature, the addition of lead before pouring, or pouring in an atmosphere of carbon dioxide. The above property is due to the power possessed by molten copper of absorbing certain gases, and of giving them off again as the temperature falls. The absorptive power of copper for carbon monoxide, hydrogen and sulphur dioxide, has been proved by Hampe. Little is known about it in respect of hydrocarbons. According to the most recent researches of Hampe, the hydrogen alone of hydrocarbons is absorbed, carbon being liberated. The above gases are contained in part in the furnace gases, in part in the gases produced in the *poling* of copper, whilst some may be evolved from the molten copper itself by the action of certain of its constituents when present. Carbon monoxide and sulphur dioxide may be present in the furnace gases, whilst hydrogen, carbon monoxide (and hydrocarbons) are amongst the gaseous products of poling. Carbon monoxide and sulphur dioxide may be evolved from the molten copper, the latter by the action of cuprous oxide on sulphide of copper, the former by the action of cuprous oxide on carbon or hydrocarbons. Lead and carbon dioxide will displace these gases from molten copper, whilst water vapour has a similar effect.

Commercial copper is frequently rendered impure by foreign bodies, most of which affect the valuable qualities of copper injuriously, even though present in small proportion; it is, therefore, of importance to know the effect of the various impurities present in copper, upon its properties.

Cuprous oxide has the property of mixing with molten copper in all proportions. It occurs in notable quantity in so-called *dry* copper; for instance, Rammelsberg found 15 to 19 per cent. of cuprous oxide in copper that had purposely been made too dry, and Eggertz found 23 to 24 per cent. of cuprous oxide in similar Swedish copper. Small proportions of cuprous oxide have no injurious effect upon copper, but larger quantities make it cold-short, and when a

certain limit is exceeded, also red-short. According to Hampe,[1] less than 0·45 per cent. of cuprous oxide has no perceptible effect, copper with this percentage commencing to show diminished toughness, but no decrease in extensibility. When the proportion of cuprous oxide reached 0·9 per cent., a small diminution of extensibility in the cold was shown, but none whilst hot. With 2·25 per cent. cuprous oxide, there is great loss of extensibility in the cold, but no red-shortness. Such copper was still equally as fit for use as ordinary cast refined copper. Distinct red-shortness only set in when the percentage of cuprous oxide reached 6·7.

Iron forms no true alloy with copper, but is irregularly distributed through its mass. Small admixtures of this metal, such as are contained in many varieties of copper, have no injurious effect upon the quality of the latter; larger quantities however are said to produce both red- and cold-shortness. Reliable information on this point, as also on the effect of varying proportions of the two metals is not obtainable.

Tin alloys with copper and diminishes its extensibility. According to Ledebur,[2] a marked diminution is only produced when the proportion of tin reaches 1 per cent.

Zinc also alloys with copper and diminishes its malleability when hot. A zinc-copper alloy containing over 20 per cent. of zinc is less malleable than copper at all temperatures.

Lead can be melted with copper in all proportions, but the greater part of it can be liquated out of the alloy by a gentle heat. According to Hampe's experiments, 0·15 per cent. of lead does not affect the malleability of copper in any way; with 0·3 per cent. of lead it becomes slightly red-short, and with 0·4 per cent. slightly cold-short. With 1 per cent. of lead, copper is unworkable.

According to Hampe, cuproso-lead oxide ($2Cu_2O,PbO$) is far less injurious than metallic lead. As much as 1·45 per cent. of this compound may be present in copper without making it perceptibly red-short, although this effect would be strongly produced by the reduction of the oxide to metal, even in the case of a far smaller quantity.

Bismuth is the most injurious impurity in copper, as very small quantities render the copper unworkable. According to Hampe, copper containing as little as 0·02 per cent. of bismuth is red-short, and 0·05 per cent. cold-short. With 0·1 per cent. the copper crumbles under the hammer at a red heat. The presence of a certain proportion of antimony somewhat counteracts the tendency of bismuth to produce cold-shortness.

[1] *Loc. cit.* 1874, 22–93; 1876, 24–6.

[2] *Die Verarbeitung der Metalle auf mechanischem Wege.*

Oxide of bismuth, which is mechanically taken up by copper, affects it like the metal, but in a less degree as far as cold-shortness is concerned. Its effect is yet further diminished if the oxide of bismuth is combined with cuprous oxide.

Arsenic in small quantities has no injurious effect upon copper. The older writers maintained that $\frac{1}{1000}$ of arsenic in copper sufficed to produce both red- and cold-shortness, but Hampe has found that 0·5 per cent. of arsenic produces no bad effects; only when the proportion of arsenic rose to 1 per cent. could a slight degree of red-shortness, but no cold-shortness, be noticed. According to the most recent researches of Hampe,[1] copper with 0·8 per cent. of arsenic could be drawn into the very finest wire. Small percentages of arsenic (0·216 per cent.) even increase, according to Hampe, the tenacity of copper, but diminish its electrical conductivity. According to Stahl[2] a small amount of arsenic is in so far beneficial in that it prevents the copper from becoming porous.

Antimony in small quantities does not affect the good qualities of copper. It has been stated that $\frac{1}{1000}$ of antimony acts injuriously on copper, and renders it useless for the manufacture of brass wire and sheet brass, but Hampe[3] has shown that copper with 0·529 per cent. of antimony can be drawn into the finest wire just as well as pure copper. Hampe finds that 1 per cent. of antimony makes copper extremely red-short, whilst an equal proportion of arsenic imparts this property only to a slight degree. Like arsenic, antimony in small amounts (0·260 per cent.) increases, according to Hampe, the tenacity of copper, but impairs its electrical conductivity.

Nickel in small quantities appears to exercise no injurious effect upon the properties of copper. Old authorities[4] state that a proportion of nickel up to 0·3 per cent. does no harm; there are no more recent determinations on this subject. According to Hampe the coexistence of nickel and antimony up to a total of 0·3 per cent. in copper does not affect the malleability of that metal in the cold.

Tellurium, which has been found by Egleston in some brands of American copper, causes red-shortness when present even in very small proportion.

According to Hampe's[5] latest experiments, silicon hardens copper without impairing its toughness or its malleability when less than 3 per cent. is present. With 6 per cent. of silicon, copper becomes

[1] *Chemiker-Ztg.* 1892, 16, No. 42.
[2] Inaugural Dissertation, Tübingen, 1886.
[3] *Chemiker-Ztg.* 1892, 16, No. 42.
[4] Plattner-Richter, *Allgem. Hüttenkunde*, p. 142.
[5] *Chemiker-Ztg.* 1892, 16, No. 42.

brittle, with 8 per cent. it is readily pulverised, and with 11·7 per cent. it is as brittle as glass. The electrical conductivity of copper is impaired by small proportions (0·52 per cent.) of silicon.

Sulphur often occurs in unrefined copper as cuprous sulphide (Cu_2S). According to Hampe it renders the metal cold-short; he finds that copper with 0·25 per cent. of sulphur is still moderately malleable, but with 0·5 per cent. it becomes very cold-short, although not red-short.

Carbon is not at all absorbed by copper according to Hampe. Up till the year 1874 all metallurgists accepted the opinion of Karsten that molten copper is capable of absorbing carbon, and that this element, which was said to be taken up in refining, in the case of *overpoling*, had an injurious effect upon the qualities of the metal.

Hampe has shown that *overpoled* copper, *i.e.* copper that has been poled for too long a time, contains no combined carbon, and that the defective properties of overpoled copper might be produced both by the reduction to the metallic state of certain metallic oxides and salts (cuproso-lead oxide, oxide of bismuth, antimoniate of bismuth, arseniate of lead) dissolved in the copper, as well as by the absorption by the metal of the gases produced in poling (carbon monoxide and hydrogen).

Phosphorus combines readily with molten copper; small proportions of this element have no injurious effect, but larger amounts (over 0·5 per cent.) render it red-short.

Salts.—Molten copper has the property of dissolving certain metallic salts which, when present in large proportion, affect it injuriously. The injurious effect of these salts is however much less than that of the metals reduced from them. That is why copper, in which such salts are reduced to the metallic state by overpoling, is much inferior to the unrefined copper in which they are still present as salts. Hampe enumerates amongst such salts antimoniate and probably also arseniate of bismuth, arseniate, and probably also antimoniate of lead, and antimoniate of copper. Certain salts, however, do the copper more harm than do the metals reduced from them; such are arseniate of copper and so-called *copper-mica*, an antimoniate of copper and nickel.

Antimoniate of bismuth, according to Hampe, only affects copper when its proportion rises to 0·7 per cent., when it produces both red- and cold-shortness. When the salt is reduced, however, a small proportion suffices to cause red-shortness. The antimony reduced from the salt diminishes the tendency of the bismuth to render copper cold-short.

Arseniate of lead is dissolved by molten copper just like cuprous oxide is. According to Hampe, arseniate of lead to the extent of 0·657 per cent., only makes copper slightly red-short, whilst after the reduction of the salt it is found to be cold-short and extremely red-short.

Antimoniate of copper in small proportions has, according to Hampe, no injurious effect upon the properties of copper; whereas copper is inclined to red-shortness when it contains 0·5 per cent. of antimony, a proportion of antimoniate of copper corresponding to the above percentage of antimony produces neither cold- nor red-shortness. On the contrary such copper proved to be superior to most commercial coppers in ductility.

Arseniate of copper, to the extent of 0·4 per cent. has, according to Hampe, no noticeable effect upon the properties of copper. A higher proportion, however, makes it cold-short, and 2 per cent. of the salt renders it red-short. The copper is improved by reduction of the salt, copper with 0·5 per cent. of arsenic being neither cold-, nor red-short.

Copper mica is an antimoniate of copper and nickel, having, according to Hampe, the formula:

$$6Cu_2O,Sb_2O_5+8NiO,Sb_2O_5.$$

This salt forms yellow scales with a metallic lustre, which are found to separate out on the surface and in the interior of many brands of copper (dry copper). According to Hampe, 0·726 per cent. of copper mica only diminishes the toughness, but not the ductility of copper, either hot or cold; with 1·44 per cent. of copper mica, copper becomes cold-short. After the reduction of the salt, however, the copper was found to be as ductile in the cold as pure copper, but somewhat harder.

Gases.—Carbon monoxide, sulphur dioxide and hydrogen are dissolved by molten copper, and are retained by it after solidification in the shape of blisters; they thus produce unsound spots in the metal, both in the heat and in the cold.

Chemical Properties

Copper is unchanged in dry air at ordinary temperatures. In damp air and in the presence of carbon dioxide, it becomes coated with a film of basic carbonate of copper (verdigris). Heated to redness in air it becomes covered with a grayish black layer of cupric and cuprous oxides, so-called copper scale. The outer part of the layer

consists of cupric, the inner of cuprous oxide the latter, on long continued heating to redness, is also transformed to cupric oxide. The scale is easily detached from copper by bending the latter, or by quenching it in water.

Copper is not attacked by water free from air nor by limewater; but with access of air it is oxidised by water that contains alkalies, acids, or various salts.

Copper is easily soluble in nitric acid, aqua regia, and boiling, concentrated sulphuric acid; dilute sulphuric acid only dissolves it with free access of air. It dissolves slowly in hydrochloric acid with access of air.

It has the greatest affinity for sulphur of all metals, and therefore combines with that element with especial energy.

If copper, rendered impure by the presence of other elements, be used as the anode of an electrical circuit, an acidified solution of copper, such as a solution of sulphate of copper (to which free sulphuric acid has been added) as the electrolyte, and a plate of copper as the cathode, the copper may be precipitated on the cathode in a state of purity, provided that a current of suitable power be employed.

Chemical Reactions of the Compounds of Copper that are of Importance in its Extraction

cuprous oxide (Cu_2O)

Cuprous oxide melts at a red heat, and is miscible in all proportions with molten copper. In the state of powder it may be transformed into cupric oxide by heating to redness in the air.

It is easily reduced to the metallic state by carbon, carbon monoxide, hydrogen and hydrocarbons. It forms silicates with silica. With oxide of lead it melts to a very limpid liquid.

When cuprous oxide is heated with sulphide of copper in suitable proportions, the whole of the copper is reduced from both compounds with the evolution of sulphur dioxide. If the quantity of cuprous oxide is too small in proportion to that of the sulphide of copper, a portion of the latter remains undecomposed.

When cuprous oxide is heated with sulphide of iron (FeS) in suitable proportions, the copper is reduced to the metallic state, whilst the iron forms ferrous oxide, and the sulphur escapes as sulphur dioxide. If the amount of cuprous oxide is too small in proportion to the sulphide of iron, cuprous sulphide, ferrous oxide and sulphur dioxide are formed, when the original substances are

present in certain proportions. If there is still less than this proportion of cuprous oxide, a part of the sulphide of iron will remain undecomposed or reduced to a lower sulphide, and combine with the sulphide of copper to form a copper matte or regulus (the *metal* of the English copper smelter). The products will thus be copper matte, ferrous oxide and sulphur dioxide.

Nitric acid first converts cuprous into cupric oxide, and then dissolves the latter.

Sulphuric acid decomposes cuprous oxide into metallic copper and cupric oxide, which latter is then dissolved in the acid.

Hydrochloric acid dissolves cuprous oxide, forming cuprous chloride, which can be precipitated as a white powder by the addition of water.

Cuprous oxide is soluble in ammonia, forming a colourless solution, which on exposure to the air becomes blue, owing to the formation of ammonio-cupric hydrate.

CUPRIC OXIDE

Cupric oxide is infusible. With lead oxide it melts, forming a slag. It can also be melted in admixture with lead. According to Karsten, a compound of oxide of lead and cuprous oxide, or an alloy of lead and copper, together with a slag containing cuprous oxide, are said to be formed, according to the proportions of the two substances.

Cupric oxide is easily reduced to metal by carbon, carbon monoxide, hydrogen and hydrocarbons.

With silica it forms, according to the experiments of Percy and Knapp, a blood-red slag containing principally cuprous oxide, in the presence of reducing gases. If these latter are excluded, a half-melted opaque mass is produced, of a brownish red colour and black surface.

Heated with sulphide of copper (Cu_2S) in proper proportions, the total copper contents of both compounds are reduced to metal with the evolution of sulphur dioxide, as in the corresponding case of cuprous oxide. With less cupric oxide, in certain proportions, copper, cuprous oxide and sulphur dioxide are produced, whilst if the proportion of cupric oxide falls below a certain limit, some of the sulphide of copper escapes decomposition.

When cupric oxide is heated with sulphide of iron in suitable proportions, as in the corresponding reaction with cuprous oxide, the copper is separated in the metallic state, ferrous oxide is formed, and sulphur dioxide evolved. With less cupric oxide than is required for

this reaction, cuprous sulphide, ferrous sulphide and sulphur dioxide are produced, and with still less cupric oxide the products are iron-copper sulphide (copper matte), ferrous oxide and sulphur dioxide.

Cupric oxide is readily soluble in acids, also in ammonia and salts of ammonia.

By the action of ferrous chloride on cupric oxide, ferric oxide, cupric and cuprous chlorides are formed; ferric chloride forms cupric chloride and ferric oxide.

Ferric sulphate acts on cupric oxide producing copper sulphate and basic ferric sulphate or ferric oxide; ferrous sulphate transforms it into copper sulphate with the production of basic ferric sulphate.

Carbonates of copper react like cupric oxide.

SILICATES OF COPPER

Silicates of copper are reduced to the metallic state by carbon in the presence of a stronger base (FeO or CaO). Silicates of copper and sulphide of iron react mutually when heated together, producing copper sulphide and silicates of iron.

Silicates of copper and metallic iron in suitable proportions interact at a red heat, producing silicate of iron and metallic copper.

SULPHIDE OF COPPER

Of the two sulphides of copper, only cuprous sulphide (Cu_2S) is of special metallurgical importance. Cupric sulphide (CuS) is not stable at high temperatures, but is decomposed on heating into cuprous sulphide and sulphur.

Cuprous sulphide is more fusible than copper itself, and melts with other metallic sulphides, even baric and calcic sulphides, to homogeneous masses, known as *matte*, *regulus*, *metal*, &c.

When cuprous sulphide is calcined in the open air (oxidising roasting) a part of the sulphur escapes as sulphur dioxide, the copper being oxidised. Another portion is further oxidised to sulphur trioxide, which converts a part of the copper oxide into cupric sulphate; the latter when more strongly heated is split up into cupric oxide and sulphur trioxide or sulphur dioxide and oxygen. By a sufficiently long continued calcination at the necessary temperature, cupric oxide is produced; with imperfect roasting the result is a mixture of cuprous oxide (reduced from cupric oxide by sulphur dioxide), cupric oxide, cupric sulphate and undecomposed sulphide.

The ultimate product of the complete calcination of compounds or mixtures of sulphides of copper and iron is a mixture of the oxides of copper and iron. If the process is stopped before all the sulphur is removed, the result is a mixture of oxides, sulphates and sulphides of copper and iron.

When sulphide of copper is roasted with substances capable of evolving chlorine, such as salt, chloride of magnesium, *abraumsalz*,[1] &c. (chloridising roasting), the copper is converted into cupric chloride and a small portion into cuprous chloride, whilst the metals originally present as chlorides are converted into sulphates, and sulphur dioxide and hydrochloric acid are evolved.

When copper sulphide is roasted with sulphates of iron or with pyrites, the copper is partly transformed into sulphate; when heated with nitrate of iron, cupric sulphate is produced.

When sulphide of copper is heated with oxides of copper the reaction already stated takes place; if the sulphide of copper is combined with sulphide of iron, the oxides of copper also attack the latter as stated above.

When mixtures of oxides and sulphides of copper and iron, containing sufficient sulphur to convert all the copper present into sulphide, are heated with carbon and silica, all the copper will unite with sulphur, and all the iron, as protoxide, with silica. If sulphur is present in excess, part of it combines with the iron, and a sulphide of copper and iron or copper matte is produced. Any copper silicate will be decomposed by sulphide of iron into sulphide of copper and silicate of iron.

When a current of air under pressure is forced through molten sulphide of copper, the copper is reduced with the formation of sulphur dioxide.

When an air current is forced through molten copper matte (sulphide of iron and copper) rich in copper, in the presence of silica, the copper is reduced to metal, the iron forms silicate (slag) and the sulphur escapes as sulphur dioxide.

When matte, rich in iron, is thus treated, the greater part of the iron can be removed out and slagged off, with the formation of a matte rich in copper.

Oxide of lead is decomposed by copper sulphide with the evolution of sulphur dioxide, metallic lead and a mixture of oxide of lead and cuprous oxide being produced. According to Percy, this reaction is

[1] *Abraumsalz*, "stripping salt," is a name applied to the upper layers of mixed chlorides of magnesium, potassium and sodium, overlying the beds of rocksalt, etc. at Stassfurt.

only complete when there is twenty times as much oxide of lead present as there is sulphide of copper.

Metallic lead has practically no effect upon sulphide of copper.

Metallic iron only partially decomposes sulphide of copper when fused with it, the products being a button containing metallic copper and metallic iron, and a ferriferous copper matte.

Zinc, too, only partly decomposes sulphide of copper, the results of the fusing of the two substances together being an alloy of copper and zinc, and a large amount of copper matte containing zinc.

Tin and antimony behave like zinc.

According to Berthier, carbon partly reduces copper sulphide at high temperatures with the formation of carbon disulphide.

According to Berthier and H. Rose, hydrogen is said not to attack sulphide of copper. More recent experiments of Hampe have however shown that at a red heat sulphide of copper is slowly but completely decomposed by hydrogen with the evolution of sulphuretted hydrogen.

Water vapour has but little effect on sulphide of copper at a red heat; at a white heat, however, the latter is reduced to the metallic state with the evolution of sulphuretted hydrogen. According to Knapp the oxygen of the water combines with the copper to form cupric oxide, which reacts with the sulphide of copper still present, forming metallic copper and sulphur dioxide.

According to Hampe carbon dioxide can slowly reduce sulphide of copper at a bright red heat, sulphur dioxide and carbon monoxide being generated.

According to Hampe carbon monoxide does not attack copper sulphide at a red heat.

Cuprous sulphide is attacked by a solution of ferric chloride, cuprous chloride, ferrous chloride and sulphur being produced; cupric sulphide forms cupric chloride, ferrous chloride and sulphur.

When copper sulphide is treated with ferrous chloride and hydrochloric acid in the presence of air, the copper forms cupric and cuprous chlorides and cupric sulphate, sulphate of iron being produced at the same time.

Ferric sulphate transforms copper sulphide into copper sulphate with the formation of ferrous sulphate.

Cupric chloride attacks copper sulphide producing cuprous chloride with the separation of sulphur.

If copper sulphide or copper matte containing iron is made the anode of an electric circuit, a solution of sulphate of copper acidified with sulphuric acid forming the electrolyte, and a plate of copper the

cathode, the copper may be deposited on the cathode by suitably regulating the current strength, whilst sulphur separates out at the anode, and iron enters into the solution of the electrolyte.

CUPRIC SULPHATE ($CuSO_4 + 5H_2O$)

Crystallised copper sulphate is soluble in 4 parts of cold water. Heated to 100° C. it loses 4 molecules of water of crystallisation, and at 200° C. the whole of it. At a bright red heat, copper sulphate is decomposed into cupric oxide and sulphur trioxide or sulphur dioxide and oxygen.

When copper sulphate is heated with carbon, metallic copper, and carbon and sulphur dioxides are formed at a low red heat; at higher temperatures, sulphide of copper and carbon dioxide are produced.

When heated with cuprous sulphide it behaves like cupric and cuprous oxides. It may be assumed that, before the temperature is attained at which this reaction occurs, the greater part of the sulphate will have been changed into oxide of copper, so that it is the latter compound chiefly that takes part in the reaction.

Copper is precipitated in the metallic state from solutions of copper sulphate by iron and zinc, and as sulphide by sulphuretted hydrogen and alkaline sulphides.

Copper sulphate solution is decomposed by the electric current, copper being deposited at the cathode, whilst the acid radical appears at the anode. If there is a solution of ferrous sulphate at the anode —the latter not being soluble—the anion (SO_4) will convert the ferrous into ferric sulphate.

CUPROUS CHLORIDE (Cu_2Cl_2)

is but slightly soluble in water, but dissolves readily in hydrochloric acid, or in solutions of the chlorides of sodium, potassium, calcium, magnesium and zinc, and of ferrous, manganous and cobaltous chlorides. From a solution of cuprous chloride, iron and zinc precipitate metallic copper, sulphuretted hydrogen and sulphides of the alkalies and alkaline earths precipitate sulphide of copper, and lime precipitates cuprous oxide.

Cuprous chloride solution is decomposed by the electric current, copper being deposited at the cathode and chlorine liberated at the anode. If cuprous chloride exists in solution at the anode it will be converted into cupric chloride by the chlorine evolved.

CUPRIC CHLORIDE ($CuCl_2$)

is readily soluble in water. It combines with cupric oxide in several proportions to form oxychlorides. From its solution iron and zinc

precipitate metallic copper, sulphuretted hydrogen and sulphides of the alkalies and alkaline earths precipitate copper sulphide, lime precipitates cupric hydrate.

When sulphur dioxide is passed into cupric chloride solution, cuprous chloride is precipitated.

The electric current deposits copper at the cathode and evolves chlorine at the anode.

Ores of Copper

The most important ores of copper are the following:—

NATIVE COPPER

This occurs in large quantities on Lake Superior in the State of Michigan, and at Santa Rita in New Mexico (U.S.A.). It is also found abundantly in Chili as copper sand with 60 to 90 per cent. of metal, and at Burra-Burra in South Australia.

CUPRITE (Cu_2O)

contains 88·8 per cent. of copper. It is abundant at Santa Rita in New Mexico and at Clifton in Arizona, and used to be found in large quantity at Burra-Burra. It has also been met with in Chili, Colombia, and Perm in Russia. *Tile ore* is an intimate mixture of cuprite and brown hæmatite.

MELACONITE OR BLACK COPPER (CuO)

contains 79·8 per cent. of copper. This mineral rarely occurs pure, but mostly contaminated with oxides of iron and manganese. Like cuprite, it is a decomposition product of the sulphur compounds of copper. It was formerly found abundantly in Tennessee, North Carolina and Virginia (U.S.A.).

MALACHITE ($Cu_2CO_4 + H_2O$)

contains 57·33 per cent. of copper, and is generally a decomposition product of sulphur-compounds of copper. It has been found in great abundance in the Urals, in Chili, at Burra-Burra, and more recently in Arizona and New Mexico.

AZURITE OR CHESSYLITE ($2CuCO_3 + CuH_2O_2$)

contains 55·16 per cent. of copper and is also a secondary product. It generally occurs with malachite, but never in such large masses as the latter. Its chief localities have been Chessy near Lyons, the

Banate, Siberia and the Urals; it has recently been found with malachite in Arizona and New Mexico.

COPPER PYRITES OR CHALCOPYRITE ($Cu_2S + Fe_2S_3$)

contains 34·4 per cent. of copper. This is the ore from which the greater proportion of the world's copper supply is derived. It often contains both silver and gold. It is generally associated with iron pyrites, often with zinc blende, galena, arsenical pyrites, fahlore, bournonite, and true silver ores. With iron pyrites it often forms such intimate mixtures that the two minerals cannot be distinguished from each other. It occurs in Spain at Rio-Tinto, and Tharsis in Portugal; in Germany, at Rammelsberg near Goslar, and Mansfield; in Austro-Hungary, at Bischofshofen, Brixlegg, Schmöllnitz and Nagybania; in England, in Cornwall, Devonshire and Wales; in Ireland, in Wicklow; in Russia, in the Urals, the Caucasus and the Altai; in France, at Chessy; in Italy, at Agordo and Massa Maritima; in Norway, at Röros and Vigsnaes; in Sweden, at Fahlun and Atvidaberg; in North America, in Newfoundland, Canada, Vermont, Virginia, Georgia, Tennessee, Alabama, Montana, and Mexico; in Cuba, Chili, Peru; in Australia, in South Australia, New South Wales, Victoria, Queensland and Tasmania, and in Africa.

BORNITE OR ERUBESCITE ($3Cu_2S + Fe_2S_3$)

contains on the average 55·6 per cent. of copper. This mineral is far less plentiful than the last-named, and is generally intermixed with it and with chalcocite. It is no doubt a decomposition product, as is sufficiently shown by its variable contents of copper, ranging between 42 and 70 per cent. It occurs in quantity at moderate depths in the copper veins of Butte City, Montana. It also occurs in the Mansfield copper schists, in Cornwall, Tuscany and Chili.

CHALCOCITE OR COPPER GLANCE (Cu_2S)

contains 79·89 per cent. of copper, and occurs in quantity in the United States of North America, especially in Montana at Butte in the Anaconda Mine, Arizona, New Mexico and Texas. It has also been found in Cornwall, Tuscany, Russia, Chili and South Australia. It does not occur in Germany as an independent copper ore.

COVELLITE OR INDIGO COPPER (CuS)

containing 66 per cent. of copper, is a rare mineral. It is said to have been found in considerable quantities in Chili.

CHALCANTHITE OR COPPER VITRIOL ($CuSO_4 + 5H_2O$)

contains 25·4 per cent. of copper when crystallised. It is a not uncommon decomposition product, carried in solution in the waters of mines that are working on deposits consisting of admixtures of sulphuretted compounds of copper with iron pyrites or marcasite.

ATACAMITE ($CuCl_2 + CuO + 3H_2O$)

contains 59·4 per cent. of copper, and occurs plentifully in Chili and Peru.

BOURNONITE ($PbCuSbS_3$)

contains 12·7 per cent. of copper and 42·3 per cent. of lead; it occurs in small quantities with other copper ores.

ENARGITE ($[4CuS + Cu_2S]As_2S_3$)

contains 48·6 per cent. of copper; it occurs in Peru and Manilla.

CHRYSOCOLLA

is a hydrated silicate of copper, containing on the average 39·9 per cent. of copper. It occurs as a decomposition product of sulphuretted copper ores, generally with malachite. It occurs plentifully in the Urals and in Chili.

FAHLORE OR TETRAHEDRITE

($4[Cu_2S,FeS,ZnS,Ag_2S,Hg_2S]Sb_2S_3,As_2S_3$)

contains between 15 and 48 per cent. of copper. It contains less copper, the higher the silver contents of the ore; the proportion of mercury is often as high as 18 per cent. It occurs in lead, silver and copper deposits in Germany, Hungary, the Tyrol and Colorado, but rarely in sufficient quantity to be worked independently for the extraction of copper.

CUPRIFEROUS ARTIFICIAL PRODUCTS

In addition to the ores of copper, copper-bearing metallurgical products of the most varying kinds, such as are obtained in the extraction of various metals, are employed as sources of copper. The most important are: cupriferous matte, regulus or metal, speiss, slags, alloys (liquation residues), oxidised slags, oxides and various liquors.

The Extraction of Copper

As is evident from the composition of copper ores and of cupriferous metallurgical products, and from the above explained chemical reactions of copper compounds, the extraction of copper can be performed by

1. Dry methods.
2. Wet methods.
3. Electro-metallurgical methods.

The dry way should be employed chiefly for ores or artificial products with high or moderate copper contents. The lower limit, below which this method will no longer prove advantageous, depends chiefly on the price of fuel.

The wet way is, generally speaking, to be employed, besides in the case of copper solutions, on all ores that cannot be profitably treated in the dry way on account of their low copper contents. Up to what limit this method is preferable to the dry way depends on the prices of fuel, of solvents, and of precipitants.

Apart from cupriferous liquors, the wet methods are only applied to metallurgical products under especial circumstances, and mostly when gold or silver is at the same time to be extracted. In this case, the percentage of precious metal will determine when wet methods should be employed.

Electro-metallurgical methods have up to the present time only been employed in a few individual instances. Various very ingenious processes (those of Siemens and Höpfner, for instance) have been devised, but, although they have been proved to be practically applicable, they have not yet been in use on a large scale for a sufficient time to enable any safe judgment to be formed as to their advantages.

On the other hand, this method is employed in a number of works for the purpose of producing pure copper from copper containing gold, silver, or other elements.

THE REFINING OF COPPER

Copper obtained, whether by the wet or by the dry way, so called *black copper* or *blister copper*, *i.e.*, crude copper, still retains a series of foreign bodies, which, as already detailed, interfere with its use in the arts. It must therefore be purified from these or *refined* by special processes, which may be either dry or electrolytic methods, and which follow directly upon the extraction of the crude copper.

Dry Methods of Copper Smelting

1. Production of Crude Copper

The most important ores of copper are the sulphuretted compounds; next come the oxides, carbonates and silicates of copper, as well as native copper contaminated by various impurities. All these ores, when sufficiently rich, are treated by smelting.

Extraction of Copper from its Sulphur Compounds

Of all the sulphuretted ores of copper, chalcopyrite is by far the most important; in this, as in bornite, sulphide of copper is chemically combined with sulphide of iron. Chalcocite is but rarely treated independently, and is mostly mixed with iron and copper pyrites and with bornite. In smelting sulphuretted copper ores we have therefore, besides getting rid of the gangue, to effect the separation of copper from iron and sulphur. The smelting operations by which these ores are treated depend mainly on the facts that iron has a greater affinity for oxygen than has copper, that copper possesses a greater affinity for sulphur than iron, and that the sulphur of cuprous sulphide has a greater affinity for the oxygen of the oxides of copper than it has for the copper.

By a sufficiently long-continued oxidising roasting it would be possible to eliminate the whole of the sulphur from the ores and to convert them into a mixture of the oxides of copper and iron. By smelting this mixture with carbon and silica it would be possible to reduce the iron to the ferrous state, and to cause it then to combine with silica, whilst the oxides of copper would be reduced to metal. Such a simple process would, however, not only yield a very impure copper, because a notable proportion of the iron would be reduced with the copper, and because the injurious constituents of the ores, especially arsenic and antimony, would be transferred to the copper in large quantities, but it would also cause the slagging off of a large amount of the copper present. In order to obtain as pure a crude copper as possible, and to avoid great loss of copper in the slags, the first step is preferably the production of a compound of sulphides of copper and of iron, free from all siliceous matter, the so-called *copper matte* or *coarse metal*, in which the copper is concentrated relatively to its percentage in the ore, whilst sulphur and iron, as also arsenic and antimony, are as far as possible removed from it; the *metal* is then smelted for crude copper, either with or without a further concentration of the copper. This compound of the sulphides of copper

and iron is produced by calcining the ore to a given point and then smelting it with the addition of siliceous fluxes; if it is then rich in copper and poor in iron, and at the same time free from any large amount of lead, as also from arsenic and antimony, or if it contains the last-named elements only in minute proportions, it is smelted direct for crude copper by one calcination, followed by a smelting operation or by simple smelting. If not it is treated by partial calcination followed by smelting, or by simple smelting, with the production of a sulphide or regulus still richer in copper, and correspondingly poorer in sulphur and iron, lead, antimony and arsenic, generally known as *blue metal, pimple metal, fine metal* or *white metal.* This substance, if sufficiently pure and sufficiently rich in copper, is smelted for crude copper, but if not it is still further enriched in copper or freed from iron, sulphur, lead, arsenic and antimony, by a repetition of the previous operations. When the matte contains silver the process of concentration is carried to a high stage so as to facilitate the extraction of the precious metal.

Crude copper is thus obtained from sulphuretted ores by a series of oxidation and reduction processes, that is to say by calcining and smelting the ores to matte or metal, and the reduction of the latter to crude copper either directly, or after-converting it to a matte richer in copper, by one or more repetitions of these processes of concentration.

The roasted ores are smelted in blast furnaces or in reverberatory furnaces, whilst the enrichment of the matte is performed either by calcination followed by fusion in blast or reverberatory furnaces, or by blowing the molten matte in converters without previous roasting. The matte is converted into crude copper either by calcination followed by fusion as above, or by treatment in reverberatory furnaces or in converters without previous calcination.

According to the type of furnace employed, the reactions are different in each case. In the blast furnace the reducing agent is carbon or carbon monoxide, in the reverberatory furnace and the converter it is sulphur. In all cases the iron is removed by slagging with silica.

BLAST FURNACE SMELTING, also known as the German or the Swedish process, consists in roasting the ores and mattes in special appliances, followed by smelting the roasted material with carbon (coke or charcoal) and siliceous fluxes in blast furnaces. By the operation of roasting, the ores are converted into a mixture of oxides, sulphates and sulphides of iron and copper. By smelting with carbon in the blast furnace the oxides of iron are reduced to the state of protoxide,

are made to combine with the silica that is added, and are thus slagged off. The sulphates of iron are decomposed by heat in part directly to oxide of iron and sulphur trioxide, or sulphur dioxide and oxygen, and in part are reduced to ferrous oxide and sulphur dioxide by carbon monoxide, the latter being converted into carbon dioxide. The oxides of copper are in part reduced by carbon monoxide to metallic copper, which abstracts from the sulphide of iron as much sulphur as is necessary to form with it cuprous sulphide, and in part are converted by sulphide of iron in the presence of carbon and silica into sulphide of copper, which combines with any other sulphide of copper present and with the undecomposed sulphide of iron to form a matte. Sulphate of copper is split up by carbon at low redness into copper and sulphur dioxide, carbon dioxide being also formed; at higher temperatures sulphide of copper and carbon dioxide are produced. The sulphide of iron that has parted with its sulphur in transforming the oxides of copper into sulphide of copper, is converted into ferrous silicate and goes into the slag; the sulphide of iron, on the other hand, that has been reduced by metallic copper goes to form a subsulphide of iron or a mixture of iron and sulphide of iron, which passes into the matte.

If the matte so produced is to be enriched, it is partly calcined and then smelted in blast furnaces with carbon and silica, the same chemical reactions taking place as in the formation of the first matte. In case of need these operations can be repeated with the second matte.

The matte obtained either by direct treatment of the ore, or by repeated enrichment, is then dead roasted (roasted sweet) and smelted in blast furnaces with carbon and siliceous fluxes to form black or coarse copper. By dead roasting, the sulphides are converted into a mixture of the oxides of copper and iron; on smelting this in the blast furnace, the oxides of iron are reduced to ferrous oxide, which combines with the silica present and is slagged off, whilst the oxides of copper are reduced to the metallic state.

Of late years attempts have been made in the United States to smelt pyritic copper ores direct for matte without previous calcination; the sulphur and iron are supposed to act as fuels, and the matte to be therefore produced with a very small consumption of carbonaceous fuel. It remains to be seen whether this process of pyritic smelting will be permanently successful.

REVERBERATORY SMELTING, also called the ENGLISH PROCESS, consists in a partial calcination of the ores and mattes, followed by a fusion of the roasted material in reverberatory furnaces with quartz

bottoms, with, in case of need, the addition of siliceous materials or ores. The ores and the mattes produced by the ore fusion and by the first concentration processes, are always roasted in special appliances, whilst the enriched mattes are converted into crude copper, either by partial roasting in special appliances and fusion of the calcined material in reverberatory furnaces, or else by fusion in reverberatories without previous calcination. In this latter case, calcination is replaced by a slow, drop by drop, fusion of the mattes in a current of air.

As in the German process, the products of the calcination are a mixture of oxides, sulphates and sulphides of iron and copper. When this is smelted in the reverberatory furnace, the oxides of copper interact with the sulphides of copper and iron, sulphate of copper with sulphide of copper, and oxide of iron with sulphide of iron. The oxides of copper act on sulphide of copper producing copper and sulphur dioxide, and on sulphide of iron producing sulphide of copper, iron, ferrous oxide and sulphur dioxide; iron oxide reacts in part with iron sulphide, forming ferrous oxide and sulphur dioxide. Sulphate of copper, if not decomposed by the heat, reacts with sulphide of copper, forming, according to the proportions of each present, either copper or cuprous oxide and sulphur dioxide. Sulphate of iron, which is only present in small quantity, is decomposed into oxide of iron and sulphur trioxide, or sulphur dioxide and oxygen. The metallic copper formed abstracts from the sulphide of iron as much sulphur as will form cuprous sulphide, whilst a corresponding amount of iron is reduced. This reduced iron either passes into the matte or reduces ferric to ferrous oxide. The newly formed sulphide of copper combines with that already present, together with the residual sulphide of iron, to form a matte. The whole of the ferric oxide present has by the above reactions been reduced to ferrous oxide, and this, together with any ferrous oxide originally present, and with that formed by the interaction of oxide of copper and sulphide of iron, all combine with the silica of the bed or of the charge to form ferrous silicate which passes into the slag.

The matte is concentrated by being partially roasted and then smelted in reverberatory furnaces. The chemical reactions hereby produced are the same as in the calcination and smelting of the ore, except that there is no gangue to be slagged off. In these concentration processes, calcination may be in part replaced by the addition of oxides or carbonates of copper.

The matte is converted into crude copper by partial roasting followed by fusion in a reverberatory furnace, or by fusion without

preliminary calcination. The roasting before fusion must be only partial, because enough sulphur must be retained in the charge to bring about the reaction between oxides and sulphides so as to reduce the copper to metal; this reaction takes place at a sufficiently high temperature, and as all the sulphur is thus evolved, the copper remains in the metallic state. The proportionately small amount of iron that still remains in the calcined matte is slagged off as ferrous oxide, chiefly produced by the action of ferric oxide upon sulphide of iron.

When matte is smelted for crude copper without previous calcination, the requisite oxidation of the sulphides of iron and copper is caused by a very slow, drop by drop, fusion of the matte whilst a current of air traverses the furnaces, and by letting the surface of the molten mass cool down repeatedly in the air current. By this means the sulphides of iron and copper are so far oxidised that, when the temperature is raised, metallic copper and ferrous oxide are produced, the latter of which passes into the slag.

The CONVERTER process, also known as the BESSEMER PROCESS, is not applied to ores, but only to mattes and generally for the production of coarse copper from them. It is a shortened English process, and consists in blowing a highly subdivided stream of air under pressure through molten matte which is contained in a pear-shaped or cylindrical converter lined with quartzose material.

Copper and iron are rapidly oxidised by the current of air, with the formation of sulphur dioxide; the oxides of copper interact with the undecomposed sulphide, forming metallic copper and sulphur dioxide; the iron is converted into ferrous oxide and slagged off by the siliceous lining of the converter. According to the duration of the blow, either matte rich in copper and with most of the iron removed, or else coarse copper can be produced. In the first case, which is rare, the converter process is divided into two separate operations, the first the concentration of the copper in a rich matte, and the second the production of coarse copper from that matte. The more usual plan is to produce by the German or the English process a matte sufficiently rich to be blown directly to coarse copper.

The matte intended to be blown is melted in cupolas and run into the converter from them; the heat necessary for the converter process is obtained from the oxidation of the iron and the sulphur.

Comparison of the Various Processes for producing Coarse Copper in the Dry Way

The German or blast-furnace process necessitates the use of carbonised fuel—coke or charcoal—and extracts the copper with comparative rapidity from the ores. In the ore fusion the slags produced are poor in copper and can be thrown away; on the other hand the products, owing to the reducing action of the carbon, are less pure than those obtained in the reverberatory furnace. The matte is poorer than the matte from the latter, because when roasted ores or mattes are fused in the reverberatory furnace, a notable proportion of sulphur is removed along with the oxides of iron, whilst in the blast furnace nearly the whole of the sulphur passes into the matte. Even the sulphur dioxide evolved by the decomposition of the sulphates of iron and copper is on its way through the furnace reduced in part by carbon monoxide to sulphur, which combines with the copper.

If the composition of the charge is faulty, containing too much or too little silica, iron is easily reduced from it, forming a solid mass (*sow*, *salamander* or *bear*) on the hearth bottom of the blast furnace.

The English or reverberatory process requires raw fuel (coal, lignite, peat or wood) and permits of the curtailment or partial avoidance of calcination by the employment of oxidised ores or carbonates in admixture with the sulphuretted ores; it yields cleaner products than the blast furnace because the sole reducing agent is sulphur and because it is possible, by proper roasting or by the addition of oxidised ores, so to conduct the operation that the most injurious constituents of the charge, namely, arsenic, antimony and tin, may be removed with a portion of the copper as *bottoms*. The matte is richer in copper because a great deal of the sulphur escapes as sulphur dioxide, and because the sulphates of copper and iron are split up into oxides, whilst the sulphur escapes in the gaseous form. On the other hand the slags from the ore fusion are not as clean as they are in the corresponding blast furnace operation and cannot be thrown away, but require special treatment to recover the copper contained in them.

The blast furnace may be employed with advantage where carbonised fuels are cheap, with ores of uniform composition, with low grade ores, which would not admit of any considerable amount of copper being slagged off, and with highly ferriferous ores, that would attack the hearth bottom of a reverberatory furnace too strongly.

The reverberatory furnace may be employed where raw fuels are

cheap, with ores of constantly varying composition, when both oxidised and sulphuretted ores are obtainable, with rich ores where loss of copper in the slags is of proportionately less importance, with impure ores containing arsenic and antimony, with siliceous and clayey ores that do not attack the hearth bottom to any great extent, and when it is important to produce pure grades of copper in the dry way.

The English process has therefore attained its maximum development where coals are cheap and where good harbours facilitate the ready importation of foreign ores and mattes of various kinds. Such places are Swansea in Wales and St. Helens near Liverpool; in these localities ores and mattes of the most varying descriptions from all parts of the world are smelted, a number of different brands of copper being produced, whilst cheap coals and cheap refractory materials are also obtainable.

There are very few places where either the German or the English process is practised in its pure form. Most copper works have striven to unite the advantages of both, the production of clean slags together with pure and rich mattes, by smelting the ores with the former object in blast furnaces, concentrating the mattes in reverberatory furnaces, and smelting the rich mattes to coarse copper in either form of furnace.

Besides the German and the English processes we have therefore to consider the combined English and German or the Anglo-German process.

The converter process, being restricted to mattes, is combined with either the German, the English, or the Anglo-German process. It is a far more rapid method than any of the others, requires but little fuel (for melting the matte), removes arsenic and antimony more completely than any of the above processes, and produces a pure coarse copper.

On the other hand, it requires a high consumption of power to drive the blowing engines, a great consumption of refractory materials (quartz and clay) for lining the converters and for repairing the lining, and evolves large quantities of sulphur dioxide, the injurious effects of which it is most difficult to overcome. (No attempts have so far been made in this direction.)

The Bessemer process is therefore indicated where power is cheap (water power), where refractory materials are cheap, where fuel is dear, and where the mattes are impure, containing arsenic and antimony. It is also of advantage in the case of argentiferous ores, from which silver bearing coarse copper is to be produced and desilverised electro-

lytically, the coarse copper of the converter being so pure that it can be cast direct into anode plates.

Although this process is still relatively recent and capable of considerable improvements, there is no doubt that under suitable circumstances it is superior to both the German and the English methods of smelting matte for coarse copper, and is destined in time to make still further headway.

The German Process of Copper Extraction

The German process consists of a series of roasting and reducing operations.

In its purest form it embraces the following operations :—

1. Calcination of the ores.
2. Smelting the calcined ore in blast furnaces for matte.
3. Roasting the copper matte.
4. Smelting the roasted matte in blast furnaces for coarse copper.

The process in this form can only be carried out with ores of sufficient purity and sufficiently high copper contents. When the ores are poor in copper, but rich in iron pyrites, or rendered impure by other elements such as arsenic, antimony, or lead, an impure matte low in copper is produced on smelting. If this matte were to be dead roasted and smelted for coarse copper, a very impure copper would be produced, which on refining would yield impure commercial copper and a large number of cupriferous by-products. In such cases the matte is accordingly only roasted so far as to leave in it sufficient sulphur to form a second matte distinguished from the first by its greater purity and higher percentage of copper. This second matte, known as *fine metal*, &c., is generally roasted sweet and smelted for coarse copper. If it is still too impure, this matte is again partly roasted and smelted, the concentrated matte so produced being then roasted dead and smelted for coarse copper. It is only in exceptional cases, for example in the presence of large quantities of lead, that it is submitted to further concentration before smelting for coarse copper, as this concentration entails great expense, serious loss of metal and waste of time.

The opposite case, in which dead roasting of the ore followed by direct smelting for coarse copper is possible, is even more exceptional than the prolongation of concentrating operations. In such instances, as have been studied by the author at small copper works in Transcaucasia, a very impure coarse copper is produced whilst much copper is lost in the slags.

In many cases where sulphuretted ores are intermixed with large quantities of earthy gangue, as also in the case of ores, rich in copper but poor in sulphur, the calcination of the ore is omitted or is employed only for the sake of removing bituminous matter; the raw ore, or the ore freed from its bituminous constituents, is then smelted for matte, so as to slag off the earthy gangue.

CALCINATION OF THE ORES

The ores that require roasting [1] are copper pyrites, bornite, chalcocite and fahlore; these are generally intermixed with iron pyrites, zinc blende, galena, and arsenical and antimonial compounds, together with quartz and earthy matter.

By calcination so much sulphur is intended to be removed as to leave just enough to combine with all the copper present in the succeeding smelting. This degree of roasting cannot be attained with exactitude in certain forms of the process (calcining in heaps, and in stalls, calcining lump ores in shaft furnaces), the roasting being as a rule carried either too far or not far enough. On smelting over-roasted ores, copper passes into the slags and some impure coarse copper is reduced; if not roasted sufficiently the matte produced on smelting contains too little copper and too much iron. As over-roasting can be corrected by the addition of raw ores to the smelting charge, whilst insufficient roasting cannot be corrected (unless oxidised ores are available), it is better to roast too much than not enough.

In addition to sulphur, arsenic and antimony ought to be as far as possible got rid of by calcination. These bodies are in part volatilised as arsenious and antimonious oxides, also as sulphide of arsenic, and in part they form arseniates and antimoniates which, in the reducing smelting that follows the roasting, are reduced to arsenides and antimonides and as such pass into the matte if in small quantity, or separate out as speiss if in large proportion. Arsenic and antimony can only be completely removed by repeated roasting and smelting; their removal is facilitated by an admixture of reducing agents, such as coal or sawdust, during calcination. The arseniates and antimoniates are thereby reduced and a portion is volatilised as metal or as oxide (arsenic in part as suboxide). The removal of arsenic is assisted by the addition of pyrites during calcination, which volatilises a portion as sulphide of arsenic. During the operation of smelting, a portion of the antimony and arsenic is volatilised in the metallic state.

When pure copper pyrites is calcined, the sulphur escapes in part

[1] The terms roasting and calcination are here employed quite indifferently, as being synonymous.

as sulphur dioxide and in part is converted into sulphur trioxide, which forms sulphates with the oxides present, these latter being decomposable at higher temperatures, till ultimately a mixture of the oxides of iron and copper is produced. If the roasting is stopped before all the sulphur is removed, as in roasting for matte smelting, the product consists of a mixture of oxides and sulphates of copper and iron together with undecomposed sulphides. If the chalcopyrite is mixed, as is usually the case, with iron pyrites, the products of calcination consist more largely of oxide of iron, sulphide of iron and basic salts of iron. If zinc blende occurs with the chalcopyrite the products will contain sulphide, oxide and sulphate of zinc. If arsenic and antimony are present in the ores, the products will contain arseniates and antimoniates together with undecomposed arsenides and antimonides; if galena is present, sulphide, oxide, and sulphate of lead will also be produced. Quartz and barytes are unaffected; carbonate of lime is converted into sulphate.

The Operation of Roasting

Calcination of copper ores is effected in heaps, in stalls, in shaft furnaces, reverberatory and muffle furnaces.

Lump ore may be roasted in heaps, stalls, and shaft furnaces. Crushed ore (fines) can only be roasted in heaps, stalls, and shaft furnaces for lump ore after they have been agglomerated; otherwise they are calcined in shaft furnaces for fine ore, reverberatory and muffle furnaces. The choice of a method depends upon the amount of sulphur present in the ore, the damage likely to be caused by the escape of the gaseous products of calcination, the market for these by-products (especially sulphuric acid), the price of fuels and the cost of labour.

Heap roasting of lump ores requires a great deal of time, with many classes of ore is imperfect in its results, admits of no condensation or utilisation of the waste gases, and, in the absence of adequate shelter, entails loss of copper by the leaching out of sulphate in solution; on the other hand, it necessitates but small prime costs, does not need much labour, and, in the case of ores rich in sulphur, but little fuel. With highly pyritic ores, which do not decrepitate when heated, it admits of the removal of sufficient sulphur, of the collection of a small part thereof, and of the formation of kernels rich in copper.

Heap roasting of *fines* necessitate the previous agglutination of these and therefore a heavy outlay for labour; in other respects it has all the disadvantages of the heap roasting of lumps. Pulverulent

fines can only be calcined in definite proportions with lump ore by being used for the floors and covers of the heaps of coarse ore.

Roasting in heaps can accordingly only be applied where there is no demand for sulphuric acid, and where the land has so little value that damage done to it by the gases evolved is of no consequence, whilst wages and the cost of fuel are high. It is employed, for instance, in the Caucasus, at Röros in Norway and in North America. It is used as an auxiliary, in the second roasting of lump ores that have undergone preliminary calcination in shaft furnaces, but that cannot be roasted completely in them on account of a deficiency of sulphur.

Roasting in stalls requires considerable time, though less than heap roasting, needs larger capital outlay and entails higher cost of labour, and is moreover injurious to the health of the men engaged in emptying the stalls. It admits of the sulphurous gases being conducted away in high stacks and thus being in part rendered innocuous, but not of their being employed in the manufacture of sulphuric acid. If the draught is properly regulated, it allows of a better and more uniform roasting and better control over the temperature than in heap roasting. Like the latter, stall roasting admits of being carried on with but little fuel in the case of pyritic ores, of the recovery of a small amount of sulphur and of the formation of kernels rich in copper. Fines can be roasted in stalls under the same conditions as in heaps.

Stall roasting is accordingly preferable to heap roasting. It is used in places where fuel is dear, where there is no market for sulphuric acid so that there would be no object in its manufacture, but where the injurious effects of the sulphurous gases on vegetation are to be limited as far as possible by drawing them off into high stacks; or again where fuel is dear and the ores low in sulphur; or where kernel roasting is found necessary; and finally where lumps, partly roasted in shaft furnaces, require a further calcination to a degree not attainable in such furnaces.

Shaft furnaces are used for ores rich in sulphur, both coarse and fine, when the gases evolved are to be converted into sulphuric acid. A necessary condition for this form of roasting is that the ores shall contain enough sulphur to furnish by its oxidation the heat requisite for the continuance of the operation; moveover the ore must not readily fuse nor sinter, nor may lump ore decrepitate at the temperature of calcination.

The advantages of shaft-furnace roasting are the condensation and utilisation of the gases evolved, and the complete saving of all fuel,

the disadvantages are the comparatively small output of such furnaces and the high cost of labour.

Under certain circumstances, especially where fuel is very dear, wages low, and the ores pulverulent, these furnaces can be employed to advantage even when no condensation or utilisation of the sulphurous gases is to be attempted. Of course in these cases, the land in the neighbourhood of the smelting works must possess but a low value. Such a case occurs in the Caucasus, where pyritic copper ore concentrates are roasted in Gerstenhöfer furnaces.

Calcination in reverberatory furnaces excludes the possibility of utilising the gases evolved for the manufacture of sulphuric acid, requires the ores to be first pulverised, and occasions considerable expense in fuel and in labour; on the other hand, it is rapid, can be adjusted with precision to the desired degree of desulphurisation, and is the best method for removing arsenic and antimony from the ore. It is applicable to all classes of ore, and has been considerably cheapened of recent years by the employment of automatic calcining plant.

It should be employed when the sulphurous vapours are not required to be utilised, but must be rendered as little injurious as possible by being conducted into high stacks; when large amounts of copper are to be produced rapidly; for ores that are not suitable to the shaft furnace on account of their ready fusibility, their tendency to decrepitate, or their too low sulphur contents; and finally when ores have to be exactly desulphurised to a definite point.

Muffle furnaces involve high costs for fuel and for wages, but admit of the gases evolved being utilised, and of exactitude in the calcination. Like reverberatory furnaces, they are only suited to fine ores. They are employed when it is proposed to manufacture sulphuric acid from ores prone to sinter or to decrepitate, and which cannot therefore be treated in shaft furnaces.

HEAP ROASTING

Two classes may be distinguished, normal heap roasting and heap roasting with the production of kernels, or kernel roasting. The object of the former is the formation of oxides and the retention of a certain proportion of sulphides; that of the latter is the concentration of the copper of the ore in a kernel of sulphides that forms in the centre of each lump, whilst the iron in the form of oxide passes into the shell that surrounds the kernel.

Normal roasting may be applied to any class of ore, kernel

roasting only to such as consist of a mixture of iron and copper pyrites, poor in copper, and are free from any admixture of gangue.

Whilst heap roasting is generally of the normal type, kernel roasting is only employed exceptionally, because of the heavy losses of copper which it entails, and indeed only when wet and dry processes are to be used in combination, the kernels being treated by smelting, whilst the shells, after removal of the kernels, are treated by wet methods.

NORMAL HEAP ROASTING

The heaps are built up on a bed of fuel in such a manner that the coarser lumps are in the centre of the pile, whilst the smaller ore, in continually diminishing sizes, forms the exterior. The heap is covered with a layer of fines or concentrates, and a similar layer is often spread on the floor of the roasting yard below the fuel, so that it may gradually be calcined.

The floor is made of granulated or crushed slag, of fines, roasted fines, or of clay. Generally a bed of clay is laid upon the slag, and a bed of calcined fines upon this. It is advisable to cut drains above the heaps, so as to prevent water having access to them, and leaching out copper sulphate. In dry climates the roasting yard is open to the air; in wet districts it is preferable to conduct the calcination, at any rate of the first and second mattes, under shelter, in a so-called roasting-shed. With ores containing more than 12 per cent. of sulphur, this suffices to maintain a roasting temperature, and the bed alone need consist of fuel; with ores containing under 12 per cent. of sulphur, there should be one or more layers of fuel in the body of the heap. This precaution is also necessary in the presence of larger quantities of arsenic, antimony and zinc. The salts formed by the calcination of these metals are best got rid of by a layer of charcoal in the pile.

The bed is best built of cord wood; in its absence, brushwood, heather, or coal can be employed. Draught channels must be left in the bed, which in case of need are made to communicate with small flues constructed in the heaps.

The size of the heaps depends on the sulphur contents of the ores, and on the time that the heap can be allowed to burn so as to maintain an uninterrupted supply of calcined ore for the smelting furnace. The higher the heap, the better and the more vigorously does it burn, but the longer is the time required for calcination, this depending far more on the height of the pile than on its area.

Higher heaps are accordingly built for ores poor in sulphur than

for the more sulphuretted ones. If there is not much time available, and the ores are rich in copper, the heaps will be lower than when the reverse is the case. In general the height of heaps varies between 5 feet 9 inches and 8 feet 3 inches; above the latter figure, the construction of the piles becomes too difficult. Ores low in sulphur should therefore be made into heaps 7 feet 6 inches to 7 feet 9 inches high, whilst with ores containing over 35 per cent. of sulphur, the heaps may be kept lower. A heap 6 feet 6 inches high requires about 70 days for its calcination; if the height be diminished, the period can be correspondingly shortened.

According to experiments of Peters,[1] the relation between the time required and the height of the heaps for a first roasting, with ores containing varying amounts of copper and sulphur, is given in the following table:—

Height in feet.	Nature of ore.	Per cent. Sulphur.	Per cent. Copper.	Days burning.	No. of sample.
5	Pyrites	39	6½	54	No. 1
5	Chalcopyrite, with little pyrites and quartz	18	14·3	41	,, 2
5	Bornite and pyrites	31	21·4	53	,, 3
5½	Same as No. 1	39	6½	66	,, 4
5½	,, ,, 2	18	14·3	50	,, 5
5½	,, ,, 3	31	21·4	65	,, 6
6	,, ,, 1	39	6½	72	,, 7
6	,, ,, 2	18	14·3	61	,, 8
6	,, ,, 3	31	21·4	74	,, 9
7	,, ,, 1, much matted	39	6½	94	,, 10
7	,, ,, 3	31	21·4	86	,, 11
7½	Copper glance and pyrites in quartz	20	23·4	54	,, 12

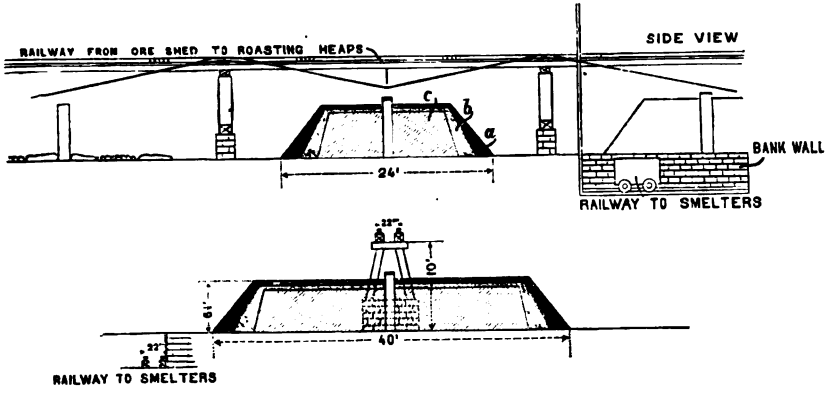
The heaps are built in the shape of a truncated square pyramid. The experience of many years in the United States has shown that, if sufficient ore is available, they should not be under 43 feet long by 25 feet 6 inches in width. A heap of these dimensions and 6 feet 6 inches high will contain about 218 tons[2] of pyritic ores, and will burn continuously for seventy days. Smaller heaps require comparatively more labour and fuel, whilst large heaps 85 feet × 42 feet 6 inches in area and 8 feet 3 inches in height, containing 300 to 400 tons, give correspondingly better results in practice. At Röros in Norway the best results are obtained with heaps of 400 to 500 tons.

The construction of the heaps is commenced by laying a bed of fuel; according to the richness of the ore in sulphur and the quality

[1] *Modern Copper Smelting*, seventh edition, 1895, p. 114.

[2] The ton here referred to is the metric ton, equal to 0·984 statute ton.

of the wood, the height of the bed may vary between 8 and 15 inches. Draught channels, 6 to 7 inches wide, must be left, at about 8 to 10 feet apart, and filled with easily inflammable material; then chimneys made of boards, sticks or old iron are built up, the number of which will depend on the dimensions of the heap. Thus a heap 43 feet by 25 feet 6 inches, holding 218 tons, should have three chimneys along the central line about 9 inches square in plan. The sides of the heaps should have such an inclination that the ore will lie without rolling down. In order to maintain a good draught and to secure a good roast, the wooden bed should project some 14 inches beyond the outside edge of the ore. In the United States the consumption of fuel is 12 cords (1 cord = 128 cubic feet), to 218 tons of ore. The best and cheapest way of dumping the ores upon the bed, is by means of waggons running on rails at a given height above the level of the yard, the rails being carried on trestles down the central



FIGS. 1 AND 2.

line of the heap. Portable turntables are placed on the track, which can be connected to lengths of movable track resting upon portable trestles. By means of this arrangement, which has given great satisfaction in the United States, the ore can be dumped at any point of the pile. The general disposition is shown in Figs. 1 and 2. The roasted ores are loaded on to waggons running on rails at the level of the charging doors of the blast furnaces.

The coarsest ore is first dumped on the bed, then the smaller sizes (raggings), and finally the fines. In the above figures, *c* is the coarse ore, *b* the raggings, and *a* the covering of fines. The latter is of special importance in obtaining satisfactory results; the best thickness can only be learnt by experience. Peters (*loc. cit.*) considers

10 per cent. of the total weight of the ore to be sufficient. It is best only to lay the covering of fines after the pile has been lit, so as not to interfere with the uniform distribution of the fire through the heap.

With ores containing large quantities of pyrites, a small proportion of its sulphur contents can be collected. In this case, after the heap has been lit for a week, hemispherical cavities are hollowed out in the cover, about 12 inches in diameter and 6 to 8 inches deep, lined with raw or calcined fines. In these a portion of the sulphur

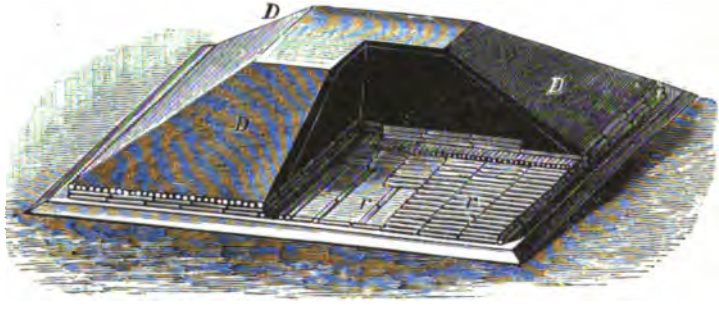


FIG. 3.

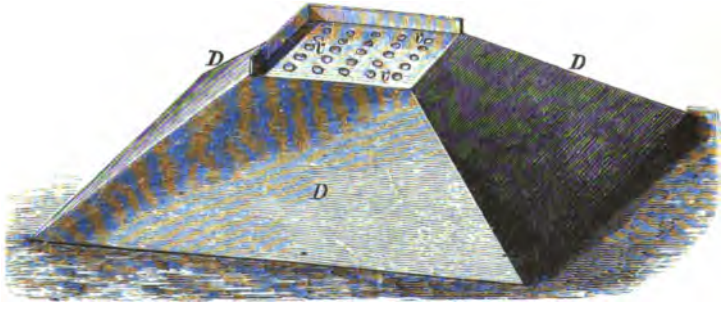


FIG. 4.

condenses, that has been distilled out from the pyrites by the hot air that has been deprived of its oxygen in the lower part of the heap, or by the hot sulphur dioxide. As the greater part of the sulphur present is oxidised, the amount collected in these cavities is but small, and forms only a fraction of a per cent. of the sulphur contents of the ore. Moreover, the sulphur so obtained is very impure, and has to be refined before it can be used, so that no profit to speak of is attainable by this method of collecting sulphur.

The arrangement of a heap for sulphur getting is shown in

Figs. 3 and 4; r is the bed of fuel, D the cover, v the cavities for collecting the sulphur.

If the temperature of the heap is too high, either on account of too big a bed, or of too strong or too weak a draught, a part of the sulphide of copper melts together with a part of the sulphide of iron, and collects as a dense layer on the floor of the heap (called heap-matte in America). This heap-matte is richer in copper than the rest of the heap, and must be roasted further by itself. When still richer in copper, it can be looked upon and treated as furnace matte.

When the roasting is skilfully conducted, it is possible to obtain 90 per cent. of the ore ready for the smelter, whilst 10 per cent. has to be roasted again; the greater part of this latter amount usually consists of fines.

Well roasted ore should have an earthy fracture and a brownish black colour; this colour indicates a large proportion of ferrous oxide, whilst a red colour indicates that very much ferric oxide is present. Sintered porous masses consist of silicates from which the sulphides have been liquated out, these latter appearing as dense fused masses with metallic lustre on fracture.

The degree of desulphurisation of ores roasted in heaps is not easy to determine, because it is both difficult and expensive to get accurate average samples. According to Peters[1] a 300 ton heap of pyritiferous chalcopyrite from Ely Mine, Vermont, showed the following composition before and after calcination:—

	Before calcination.	After calcination.
Sulphur	32·6 per cent.	7·4 per cent.
Copper	8·2 „	9·1 „
Insoluble residue	27·0 „	31·1 „

Of the copper present, there was in the form of

Sulphate	1·3 per cent.
Oxide	2·1 „
Sulphide	5·7 „

Imperfectly roasted pieces are picked out and calcined a second time, the second calcination being generally performed under cover; this second calcination is, generally speaking, sufficient. With ores that are difficult to roast, a third fire may be required for such lumps as were not properly calcined in the second; the second and third calcinations last only a few weeks as a rule.

[1] *Op. cit.* p. 133.

The consumption of fuel varies within wide limits, depending upon the percentage of sulphur in the ore, the size of the heaps and the number of calcinations required. In the United States, with pyritiferous ores, burnt in heaps of 218 tons, 5 cords of wood are consumed for every 100 tons. In the Upper Harz, copper pyrites with an average of 18 per cent. of metal was roasted in heaps of 108 to 117 tons at one operation, lasting 8 to 13 weeks, with a consumption of 18 to 24 tons of wood. At Fernezely near Nagybanya in Hungary, whilst the author was there, pyrites were calcined in heaps of 120 to 240 tons, consisting of three layers of a mixture of coarse ore and fines. For each 10 tons of ore, 406 cubic feet of wood and 137 bushels of charcoal were used; at present heap roasting has been replaced at this locality by shaft-furnace roasting. At Röros in Norway, pyritic ores with 5 per cent. of copper and 35 per cent. of sulphur are roasted in heaps 5 feet 9 inches high, 23 feet wide and 49 to 98 feet long, containing not less than 250 tons; 500 tons are found to give the best results. A roasting lasts 5 to 6 weeks and reduces the sulphur contents to 5·6 per cent.

A peculiar method of roasting is that introduced in 1888, at the

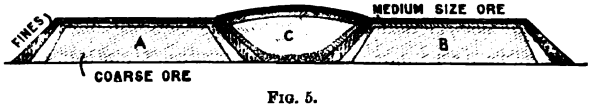


FIG. 5.

works of the Canadian Copper Company at Sudbury in Ontario, by Peters and MacArthur, and known as the V-method (Peters, *loc. cit.*). It consists in uniting two heaps that are burning, by the introduction of a third heap between them. After two adjacent heaps have been burning for a fortnight, a third heap is built between them; a bed of wood is laid between the longer sides of these two first heaps, and the ore is dumped upon it as quickly as possible. The arrangement is shown in Fig. 5, where A and B are the two original adjacent heaps, and C the heap erected between them.

After the latter has been lit, the neighbouring side walls of the older heaps also take fire and calcine thoroughly. The percentage of imperfectly roasted ore is therefore much less than in the case of the ordinary method, whilst the capacity of the roast-yard is correspondingly increased. This system is said to have given great satisfaction.

KERNEL ROASTING

This method is only applicable to mixtures of pyrites and chalcopyrite that are free from gangue and do not decrepitate. It is

performed by greatly prolonging the operation of calcination by means of checking the draught. In this process, the sulphide of iron is directly oxidised in consequence of the great affinity of iron for oxygen, whilst the sulphide of copper remains undecomposed on account of the great affinity between copper and sulphur. The heat developed by the oxidation of the sulphide of iron suffices to melt the sulphide of copper; the latter penetrates through the porous crust of oxide of iron produced by the oxidation of the sulphide of iron, into the interior of the lumps and there unites with the still undecomposed sulphides. Underneath the porous crust of oxide of iron there is thus formed first of all a thin dense layer of the colour of chalcopyrite, surrounding the still undecomposed ore. This layer advances into the lump as the crust gets thicker, and shows where in contact with the crust, first a violet colour, becoming blue, then gray, and finally bronze coloured. These various rings gradually

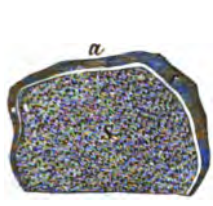


Fig. 6.

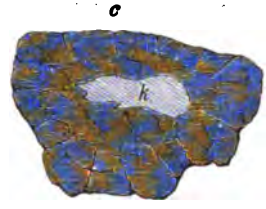


Fig. 7.

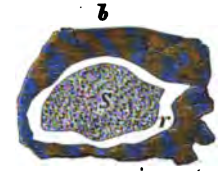


Fig. 8.

advance into the interior of the lump, which finally also becomes bronze coloured. The bronze-coloured kernels consist of sulphide of copper with but little sulphide of iron. As soon as all the latter has, however, been completely oxidised, the former may also be attacked if the calcination is carried too far. Cuprous oxide is thus formed, and this reacts with a portion of the sulphide forming metallic copper and sulphurous anhydride. The advance of the sulphides at various stages of the roasting is shown in Figs. 6 to 8.

In Fig. 6, the lump of ore has been exposed to calcination for a short time only; a is the porous crust of oxide of iron, r is the ring of fused sulphides, and S is the kernel consisting of undecomposed sulphides. In Fig. 7, the roasting has been continued for some weeks the letters bearing the same meaning as in Fig. 6; the kernel of undecomposed sulphides has grown smaller, whilst the ring of fused sulphides has increased in breadth. Fig. 8 shows a piece of ore when the roasting is completed; the kernel of undecomposed sulphides has disappeared and is replaced by a small kernel (k) of fused sulphides of the colour of chalcocite, surrounded by a porous reddish-brown crust

(*c*) of oxide of iron. If the roasting were now carried still further, a kernel very rich in copper would be segregated, and finally metallic copper would be reduced from it.

The oxidation of the sulphide of iron in the interior of the lumps of ore is brought about chiefly by sulphur trioxide in a state of vapour produced during the roasting, the interior of the lumps being filled with vapours of this gas and of sulphur.

If the roasting is properly conducted, the products will be kernels containing from 7 to 60 per cent. of copper according to the richness of the ore, and crusts carrying only a few per cents. of copper as sulphate and oxide. The kernels must be separated from the crusts by hand, and it is impossible to prevent some portions of the sulphides from adhering to the crusts.

The kernels are treated in the dry way; if their copper contents are low, they are smelted for matte with or without previous calcination; if high they are roasted dead and smelted for coarse copper. The crusts are treated in the wet way, the sulphate of copper being leached out, and the copper in solution precipitated by means of iron.

Kernel roasting has been employed at Agordo in the Venetian Alps, Wicklow in Ireland, Foldal in Norway, and Kedabeg in the Caucasus. It has been abandoned in most places on account of its slowness, of the serious loss of copper due to the retention of oxide and more particularly of sulphide of copper in the crusts, and of the high cost of separating the kernels from the crusts, which latter operation can only be performed by hand. It may, however, be of value in uncultivated districts where fuel is dear and labour cheap, where cupriferous pyrites can find no market, and cannot be employed in sulphuric acid manufacture.

At Agordo, where the author first studied this process, cupriferous pyrites with 2 per cent. of metal was treated by it. The mineral was laid upon a bed of wood so as to form heaps of 250 to 300 tons, 23 feet long, 20 feet broad, and 8½ feet high. The draught was checked by means of walls of small ore built into the heap itself, and by covering the latter with two layers, the first of small ore, and the second of leached crusts, each 1 foot in thickness. The bed of wood was laid upon a foundation of leached crusts, filled into a pit in the ground 6½ feet deep. Logs of wood were set in the latter, 3 feet apart; when the heap was lit, these logs caught fire and burnt, thus forming airways for the admission of air into the heap. The walls for checking the draught only started about 2 feet above the level of the ground, and were run parallel to the longer side of the heap. In the upper

layer of the covering, hemispherical cavities were made for the collection of sulphur.

Fig. 9 shows the arrangement of such a heap; *a* are the logs of wood inserted in the crusts; *b* are stones to support the covering; *c* are the walls of small ore; *d* are the cavities for the collection of sulphur; *k* is the covering of small ore; *i* of leached crusts. The heap was lit from the four corners; after 5 to 6 weeks sulphur began to collect in the cavities. It was ladled out and refined by remelting in iron pans. It continued to condense up to 6 weeks before the end of the calcination, which lasted in all 8 to 10 months. A 200 ton heap would consume 212 cubic feet of wood. When the roasting was finished the heap was allowed to cool for a month, and the lumps were then sorted by hand, boys being employed. Some of the sulphides necessarily remained adherent to the crusts, whilst all of the latter material was not separated clean, on the other hand, from the kernels. The products were 87 per cent. crust and 13 per cent kernels, containing on the average 6 per cent. of copper, the poorer ores yielding kernels with 3·45 per cent., and the richer ores kernels with 9 to 10 per cent. of copper.

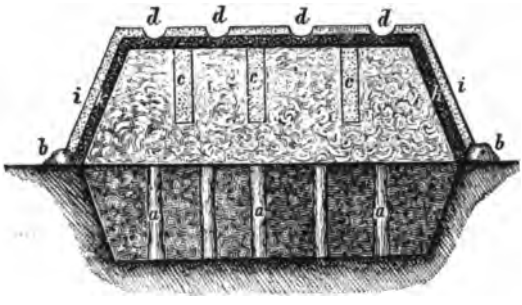


FIG. 9.

In Norway, ores with ½ to 1 per cent. of copper yielded kernels with 7 to 15 per cent. of metal.

In the Caucasus, where the author introduced kernel roasting, ores containing 7 to 10 per cent. yielded kernels with 35 to 45 per cent. of copper after six months roasting. The crusts contained 3 to 4 per cent. of copper, whereof 2½ to 3 per cent. was in the form of sulphate and ½ to 1 per cent. in that of oxide.

HEAP ROASTING OF FINES

can only be performed when these are first agglomerated into lumps and then thoroughly dried. The cementing material used is a solution of green vitriol (sulphate of iron) either by itself or with the addition of a little clay. As this agglomeration requires a considerable outlay for wages, this method is never used except when the object is to convert the copper into sulphate for its extraction in the

wet way. Otherwise it is preferable to calcine the fines or concentrates in shaft, reverberatory or muffle furnaces, or to smelt them raw. This process of agglomerating concentrates into lumps, and heap roasting them so as to form sulphate of copper was employed, *e.g.* at Agordo, for concentrates of cupriferous pyrites poor in copper.

REMOVAL OF BITUMEN FROM COPPER ORES BY HEAP ROASTING

Certain cupriferous schists contain bituminous matter that has an injurious effect upon the smelting process, and which must therefore be removed before the ores can be smelted; the only practicable way of removing this bitumen is by roasting the ore in heaps. Such ores are the copper-schists (*Kupferschiefer*) raised from the mines of the Mansfeld Company; they are bituminous marly schists with 1·8 to 3·7 per cent. of copper and a small proportion of silver (0·53 to 0·58 per cent. of the copper contents). They are roasted in heaps merely with the object of getting rid of the bituminous matter, because this would otherwise entail a larger consumption of fuel on smelting in the shaft furnace and would make the slag difficultly fusible and richer in copper. But for this, the schists would be smelted raw so as to collect the small percentage of copper that they carry into a matte. Formerly the schist used to be burnt in heaps of 1,200 to 1,500 tons, an operation that occupied about six months; now however long narrow heaps of at most 600 tons are employed, which can be completely roasted in four weeks, so that the amount of working capital engaged has been considerably diminished. No bed of fuel is required, as there is sufficient bitumen in the copper schists to maintain combustion; to start the fire a layer of brushwood is laid round the foot of the pile. The mine-smalls are made into briquettes by being mixed with tar and moulded in a press, and these briquettes are intermixed with the pieces of schist in the heaps.

This burning or calcination does not produce any alteration in the chemical composition of the metallic sulphides contained in the schist, as in the case of ordinary roasting, but only frees the schist from bitumen, and at the same time expels moisture and carbon dioxide from it.

ROASTING IN STALLS

This method is applied for both normal and kernel roasting. Stalls may be classified as being with or without beds of fuel, open or closed, with or without flues and stacks. The horizontal section of stalls is rectangular, square or circular; the latter form is the rarest. It is employed for roasting mercurial copper ores in

Hungary (Stephanshütte, near Göllnitz), and for pyritic copper ores at small works in Transcaucasia (Allawerdi, Karabach). The rectangular shape is generally preferred because such stalls take up less space when grouped together, the products of combustion are more easily led away and they are more convenient for filling and emptying.

The conditions for stall roasting are the same as for heap roasting; the former however requires less time if the draught is properly regulated, and allows the gases generated to be carried off by stacks. The advantages of rapid and uniform roasting can however only be obtained when stacks are employed and the draught is carefully attended to. Stalls with an imperfect draught, such as are often found, give results much less favourable than heap roasting, hence such stalls have often been abandoned in favour of heaps. The larger the stalls, the more difficult is the proper regulation of the draught, hence stalls should be of moderate dimensions to ensure rapid and good roasting. Stalls without flues or stacks need as much time as does roasting in heaps, and their only effect is to protect the burning pile against wind and weather, to keep the heat together better, and to prevent the sulphate formed from being leached out by rain.

Hence instead of large stalls, a greater number of smaller stalls, with flues leading into stacks with a good draught, should be employed; these stacks should be from 66 to 82 feet high, insufficient height being indicated by the undue prolongation of the roasting. Stalls, that are open above, are closed airtight by a layer of smalls or concentrates; in some places a sheet-iron cover is used. The open front side is closed by a temporary dry-stone wall, provided with openings for the admission of air or with a similar wall constructed of large lumps of ore or of matte. It is also advisable to have air openings in the side walls, which are in communication with an air passage running the length of each wall. The back of the stall forms a part of one of the side walls of the flue leading to the stack, there being a series of rectangular openings that connect the stalls with the main flue. In all large works two rows of stalls are built back to back so as to have the main flue between their rear walls. The dimensions of such stalls will vary within certain limits with the sulphur contents of the ores. Ores rich in silica and poor in sulphur require higher and wider stalls than do ores rich in sulphur and poor in silica. In Montana the best dimensions for ores with a medium proportion of pyrites (30 per cent. of sulphur) have been found to be: length 8 feet in the clear, width 6½ feet in the clear, height 6

feet. Such stalls take 20 tons of ore, which can be completely roasted in 10 days. With the above proportion of sulphur, larger stalls are found to take more time and give inferior results.

As an example of the above-described small stalls with stacks,

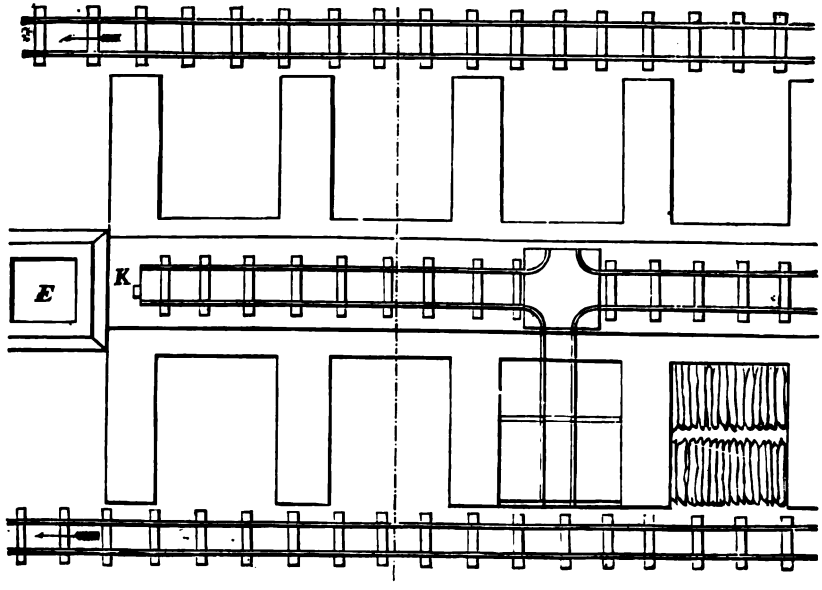


Fig. 10.

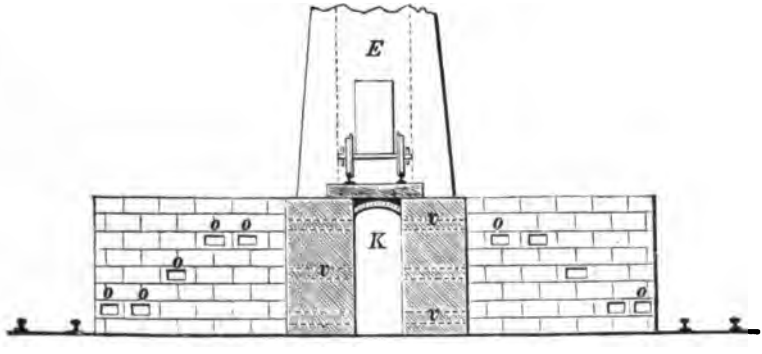


Fig. 11.

those used by the Parrot Silver and Copper Company of Butte Montana, may be instanced, which the author had an opportunity of examining; they are shown in Figs. 10 and 11. They are built of slag bricks, without any ironwork for anchoring, and are arranged in

two rows so that the main flue runs between the back walls of these rows. The stalls are filled in the manner described under heap roasting, by means of a high level railway track and portable turntables and branch tracks.

In the figures, K is the flue built with clay mortar, running between the two rows of stalls, 2 feet wide in the clear which leads the products of combustion to the stack E, 82 feet high, 3 feet 6 inches square inside measurement. The flue is covered over by a brick arch; together with the stack it suffices for the requirements of two rows, each of 25 stalls. Each stall is 8 feet long, 6 feet 6 inches wide and 6 feet high inside measurements; *v v v* are small flues in the rear wall, that convey the gases produced during calcination into the main flue K. There are nine of these flues in each stall at three different levels, as shown in Fig. 11; each flue is 6 inches wide by 2 inches high. There are similar openings *o o o* in the side walls of each stall. With the exception of the end walls of each row, in which these apertures are in direct connection with the air, these openings are supplied with air by means of longitudinal flues in each wall, which flues are divided lengthways by a partition, so that the air makes its way along them into each pair of stalls that have a common side wall. These longitudinal flues do not continue into the main flue. The draught is regulated partly by a damper in the latter, and partly by more or less blocking the flues in the rear wall by means of bricks.

Each stall holds 20 tons of ore, which is calcined in 10 days.

On the level floor of the stall, three channels parallel to the longer side of the stall are built with lumps of raw ore and filled and surrounded with easily inflammable wood. The bed of wood proper, which should consist of proportionately small pieces, is then laid over and between these channels, and the ore is charged upon it. From time to time logs of wood are placed against the side and back walls to ensure a uniform propagation of the fire. The coarsest lumps of ore come first, upon these smaller ores, then a cover of fines, and a second cover of roasted fines. A layer of chips of wood is often laid beneath the raw fine ore to promote its calcination. The front of the stall is closed by a wall of lumps of raw ore or of bricks laid dry, the necessary air openings being left in either case.

When calcination has been started by lighting the stall, and the draught is duly regulated, the normal progress of the roasting may be recognised by a slow rising of the covering. The volume of the ore is increased by calcination; since it cannot produce lateral expansion, as in the case of heap roasting, because the walls prevent it,

the mass of ore has to expand vertically upwards. The total amount of such expansion is about 1 foot in the case of pyritic ores, and may be as much as 3 inches in 24 hours.

When the draught is properly regulated the results are identical with those of good heap roasting. If the stack is low and the draught therefore feeble, the operation takes correspondingly longer. With pyritic ores the consumption of wood is very small; in the above stalls, with ores containing 30 per cent. sulphur and 25 per cent. silica, it amounts to $\frac{1}{5}$ cord for 20 tons or 0·01 cord per ton.

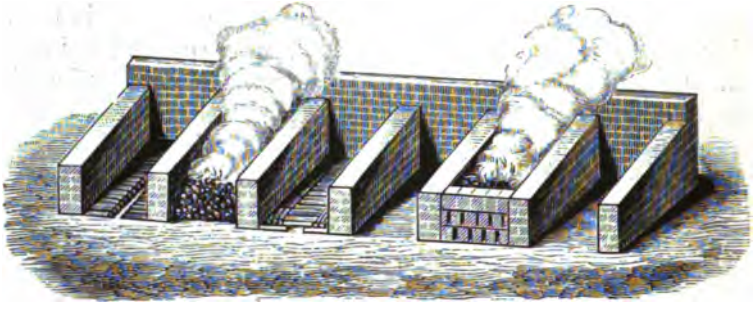


Fig. 12.



Fig. 13.

Larger stalls with a horizontal floor and without stack were formerly, and still are, often used, although calcination is effected less perfectly and with greater consumption of fuel in them than in the smaller stalls fitted with flues and stacks. These larger stalls were used, *e.g.* in Sweden, where they were 13 feet 6 inches to 15 feet long, 10 feet to 11 feet 6 inches wide and 4 feet to 6 feet high. The ores contained in addition to a small amount of copper pyrites, iron pyrites, and blende at Atvidaberg, together with galena at Fahlun. The roasting, with one fire, took 4 to 6 weeks, each stall holding about 75 tons of ore, and using 283 cubic feet of firewood. The arrangement of a row of stalls of this type is shown in Figs. 12 and 13; in the

former the front of the stall is wholly, in the latter partly, open. In either case the opening is closed by a temporary wall, as shown in Fig. 12, whilst the gases evolved escape through the covering.

Stalls worked without a bed of fuel, so-called *Wellner's* or *Freiberg* stalls, have an inclined floor, and may or may not be provided with a stack. A stall of the latter type is shown in Fig. 14. It consists of two halves *A* and *B*, which are alternately charged with ore through the doorway *o*. In each of the narrower sides there are four fire-grates *r*, by means of which the ore is fired. When the stalls are being filled, channels are formed in the prolongation of these grates by means of lumps of raw ore, through which the products of combustion pass into the heap to escape through the covering of the ore. After the stall is filled, firing is kept up until the bottom layer of ore has ignited. If the ore is to be roasted more than once the other half of the stall is left empty for the next calcination. Each half is 8 feet

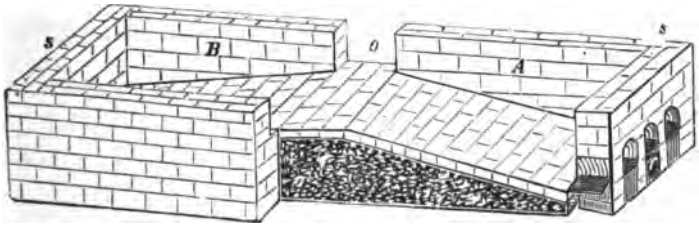


FIG. 14.

to 10 feet long by 10 feet to 11 feet 6 inches wide in the clear, with four fireplaces.

When a stack is to be used, a vertical flue descends from the point where two halves meet, which communicates with the stack by means of a horizontal flue. These Wellner stalls have the advantage that any kind of fuel can be used in them ; on the other hand, they are difficult to fill and empty unless a high-level railway track is used. Although they are well suited to places where no wood is obtainable for calcination, they have made their way into but few localities.

When calcination is required to be effected very slowly, as in kernel roasting or in converting sulphides of copper into sulphate, very large stalls are, on the other hand, used. A characteristic form for kernel roasting is the *Styrian* stall, shown in Figs. 15 and 16, which was formerly in use at Agordo. Its length was 384 feet, its width 14 feet, and its height 8 feet. The walls were 5 feet 3 inches thick, and in them were flues *l*, through which the expelled sulphur made its way into receivers *c* ; the receivers were closed by doors *p*, and twelve flues opened into each one. The floor *a* of the stall was

formed, as in the corresponding form of heap roasting, of leached-out ore crusts, with logs of wood set in them. In the floor there were a series of air channels, which were covered with slabs of stone while the stall was being filled. The filling was done at first through doors left in the walls, and later from above. A layer of wood *n* was first laid on the floor; upon this wooden chimneys were erected, communicating with the air channels, and after the stall had been lit they were

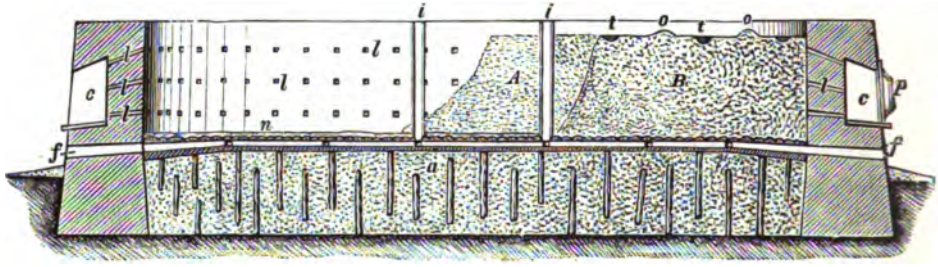


FIG. 15.

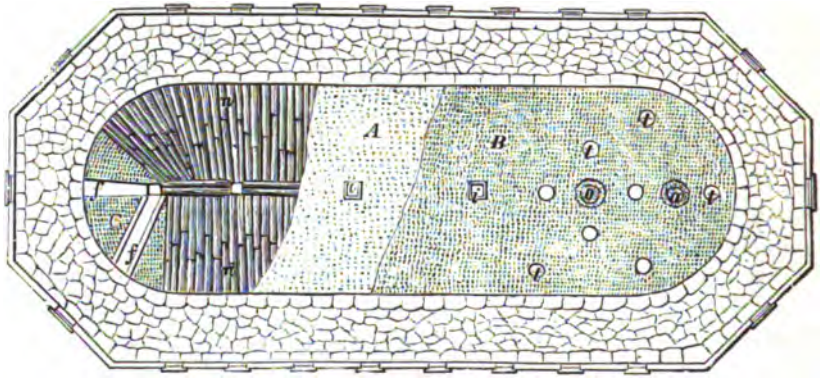


FIG. 16.

filled up with fines. Upon the lumps of ore a layer of ore fines was laid, and upon this another cover of leached ore crusts, in which were hemispherical cavities for the collection of sulphur. The time of calcination in these stalls was six to eight months.

ROASTING IN SHAFT FURNACES

This method presents advantages over heap and stall roasting in that it can be executed without fuel in the case of ores containing a suitable amount of sulphur, that the products of combustion are suited to the manufacture of sulphuric acid, and that it can be

worked continuously. It has, therefore, almost entirely displaced heap roasting in civilised countries, where sulphur dioxide cannot be allowed to escape freely. In order to be applicable to sulphuric acid manufacture, the products of combustion must contain at least 5 per cent. of their volume of sulphur dioxide. This method can be used for both lumps and ore fines.

CALCINATION OF LUMP ORES IN SHAFT FURNACES

Lump ores to be roasted in shaft furnaces must contain sufficient sulphur to continue burning by themselves, and may neither frit nor decrepitate at the temperature of calcination. The richer the ores are in sulphur, the more complete is the calcination. Copper ores containing lead (*e.g.*, those of Rammelsberg, near Goslar, with sulphur 27 per cent., copper 5 per cent., lead 9 to 10 per cent.) cannot be so far desulphurised in these furnaces as is necessary for matte smelting; they, therefore, require a second roasting in heaps. Pure copper pyrites is not suitable, because it is too readily fusible, decrepitates in the heat, and does not evolve sufficient sulphur dioxide. The ores best suited to this class of calcination are pyritic ores not too rich in copper (not much over 10 per cent.), like those from Rio Tinto with 3 to 4 per cent. of copper and 48 per cent. of sulphur, those from Vermont, Canada, with 3·5 per cent. of copper and 45 per cent. of sulphur, and those from Rammelsberg with 7 to 8 per cent. of copper and 41 to 42 per cent. of sulphur.

Ore fines can only be roasted in shaft furnaces for lump ore if they are first agglomerated into lumps, but are far better and more cheaply roasted in shaft furnaces for pulverulent ores.

When fuel is very dear and wages low, copper ores rich in sulphur may also be roasted without utilising the products of combustion for sulphuric acid manufacture. (Oxford Nickel and Copper Company, Sherbrooke, Quebec, and in the Caucasus.)

The shaft furnaces in use are either so-called pyrites burners or kilns.

Pyrites burners are low furnaces, about 3 feet high, in which the ores lie upon grates consisting of movable bars. Kilns, which are simply called shaft furnaces in some places, are higher (up to 15 feet in height) with or without grates. In pyrites burners, ores rich in sulphur, in small pieces (bean to walnut size, not exceeding 1·2 inches cube), are roasted in layers of between 15 and 24 inches in depth, whilst ores poorer in sulphur, in lumps up to 2·5 inches cube, are roasted in deep columns in kilns.

Pyrites burners are employed in most sulphuric acid works for the

roasting of pyrites; each furnace will treat up to ½ ton in twenty-four hours. The older form of pyrites burner, such as is used at the works at Oker for roasting the pyritic ores of Rammelsberg, is shown in

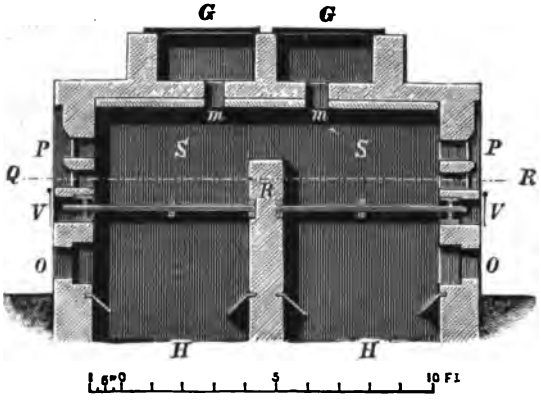


Fig. 17.

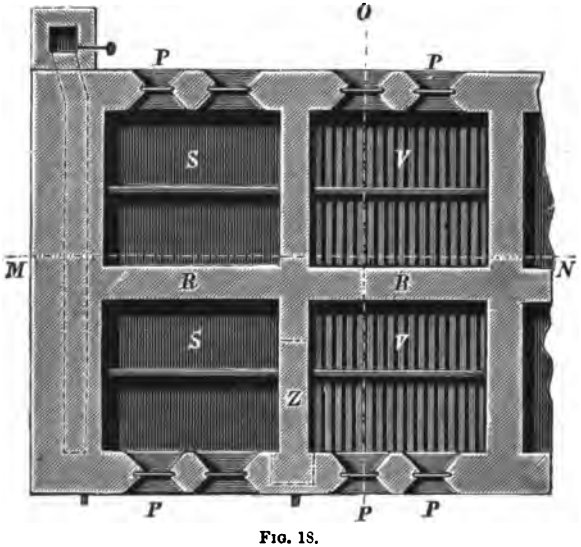


Fig. 18.

Figs. 17 to 19. Eight burners are united in one block, in two rows back to back. Each furnace is 3 feet 3 inches high in the centre, 5 feet 9 inches broad, and 4 feet 9 inches deep in the clear. The rear wall *R*, which is common to a pair of furnaces, has only the height of the charge, whereby variations of temperature in each pair of communi-

cating furnaces at various stages of the process can be equalised. The floor of the furnace is formed by the grate *V*. This grate consists of bars laid on edge, which can be turned through 90° either way by means of a key. By turning the bars, the space between them is increased and the roasted ore drops through the grate out of the furnace body into a passage below the grate, in which cars are ready to receive it. The ore is charged through the upper row of the openings *P*, which are closed by means of cast-iron doors. (A more convenient arrangement, which is often adopted, consists in charging through openings in the roof.) Both sets of openings *P* serve for the introduction of tools to prevent fritting and to loosen the layer of ore. Air enters through the apertures *O* beneath the grate, whilst the products of combustion escape through *m* into the flues *G* and thence pass to the sulphuric

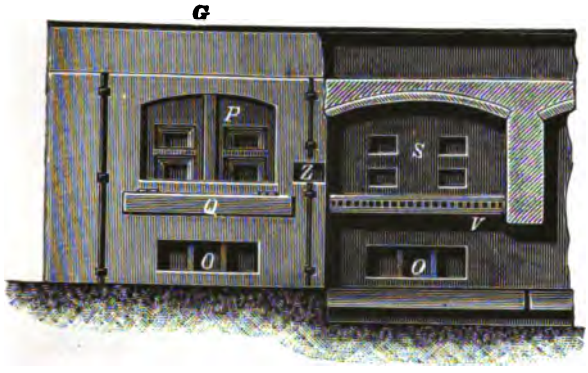


FIG. 19.

acid chambers. In front of the grates are doors *Q* hung on hinges that are opened when the grate bars are turned to empty the furnace. *Z* is a recess in the wall lined with cast-iron plates and fitted with cast-iron doors, made to receive cast-iron boxes charged with Chili saltpetre (nitrate of soda) and sulphuric acid, in order to generate the nitric acid required in sulphuric acid manufacture. This recess is connected with the flue *G* by means of a short vertical flue, through which the nitrous gases make their way into the acid chamber. At Oker a block of eight pyrites burners calcines daily $3\frac{1}{2}$ tons of ore, or 34 lbs. of ore for each square foot of grate area. The newer burners erected here possess three rows of working doors.

The design of English pyrites burners, faced with cast-iron plates, is shown in Figs. 20 to 22, after Lunge, drawn to a scale of $\frac{1}{50}$. In these *v* are the working doors for charging pyrites, *x* for stirring the ore, *z* the outlet for the sulphurous gases. The doors for the openings

v and *x* slide on grooved rails cast on the iron plates that cover the furnace.

Pyrites burners work continuously, raw ore being charged in proportion as burnt ore is drawn off. A furnace is emptied and charged at Oker every sixteen hours. The proper regulation of the air current is of great importance. An amount of air must pass

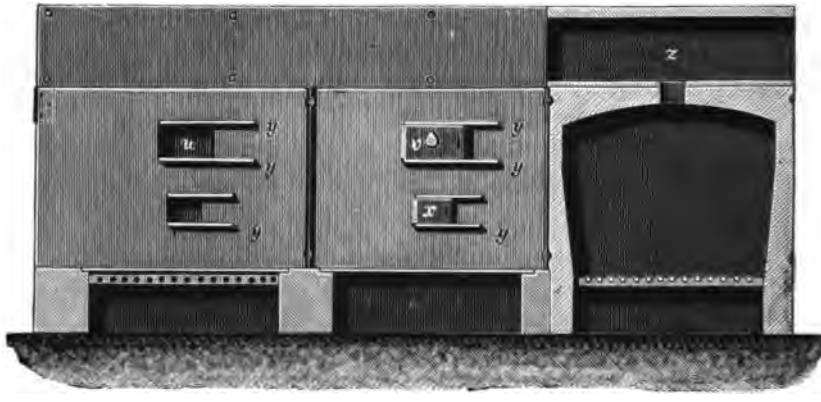


FIG. 20.

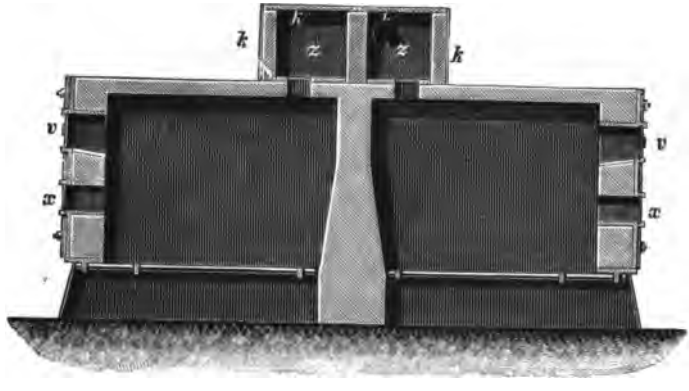


FIG. 21.

through the grate not only sufficient for the calcination of the ore, but also sufficient to convert the sulphur dioxide into trioxide in the lead chamber, together with a certain excess, the oxygen of which is to oxidise the nitric oxide contained in the gases escaping from the lead chamber (requiring about 5 per cent. of oxygen in the escaping gases) in order that the latter may be retained as nitric peroxide in the Gay Lussac tower. If the products of calcination contain too much

air they will be too poor in sulphur dioxide; if too little air is present, the calcination will be imperfect and the ores will frit together or even melt. At the same time too little sulphuric acid will be produced in the lead chambers, and nitrous gases will be wasted.

The air current is regulated by dampers in the flue of each furnace, and in the main flue or in the outlet flue from the lead chamber.

In the pyrites burner at Oker the bed of ore is 18·5 inches in depth, the largest piece being 1·2 inches cube. When suitable burners and ores are employed, the sulphur contents of the roasted ore need not exceed 4 per cent.; at Oker the sulphur is brought

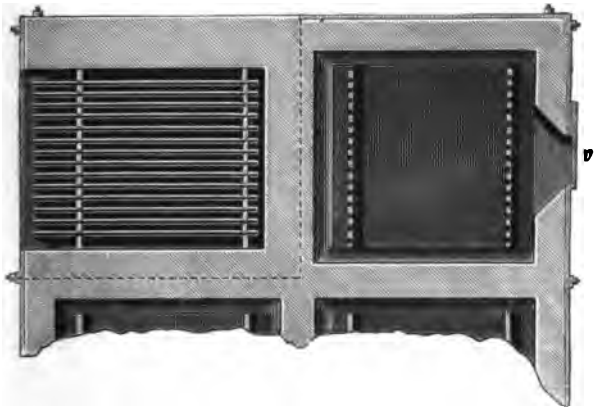


FIG. 22.

down to 5 or 6 per cent., corresponding to the proportion of copper (6 to 9 per cent.) in the ore.

In order to start a pyrites burner, it is dried at a gentle heat; it is then filled to within 3 inches of the top with roasted ore, upon which a fire is lit until it becomes red-hot, the products of combustion being meanwhile led off through a temporary chimney. This latter is then removed, and raw pyrites is charged, which takes fire and the operation proceeds.

KILNS

Kilns or shaft furnaces keep the heat together better than pyrites burners, on account of their greater height, which varies between 5 feet and 15 feet. The section is generally rectangular or square—3 feet 3 inches to 5 feet wide by 5 feet to 8 feet long, inside measurements; in many cases the shaft widens a little, going upwards. Kilns are particularly suited to the calcination of ores, too poor in sulphur

to be burnt in pyrites burners, which would only calcine such ores very imperfectly, whilst the temperature would fall so greatly each time the furnace had to be emptied and re-charged that roasting could not continue unaided. Only moderately large pieces, about 2·4 inches cube, can be roasted in kilns, because smaller ore would pack too close and stop the draught. According to the nature of the ore, 1 to 2 tons can be roasted in 24 hours.

The construction of the kilns at the Freiberg works is shown in Figs. 23 and 24. *S* is the shaft, about 9 feet 6 inches high, rect-

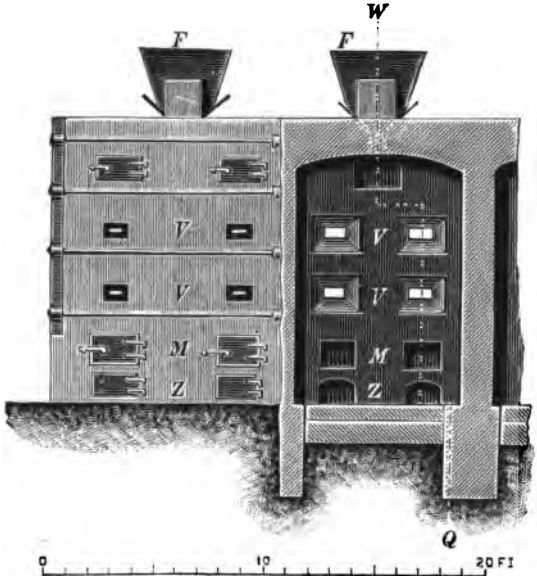


FIG. 23.

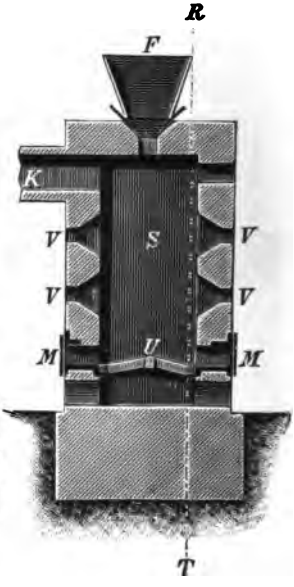


FIG. 24.

angular in section, about 4 feet 1 inch wide by 7 feet 3 inches long. The ores are charged by means of a hopper, closed by a slide, set over an aperture in the arch of the furnace; better than a slide is a cone or bell, the raising of which opens the hopper. The ores rest on the saddle-grate *U*, and air enters through the openings *Z*. The products of calcination escape through the flue *K* in the rear wall into the main flue, which is common to a set of kilns, and which carries the gases to the sulphuric acid chambers. The calcined ore is drawn out through the openings *M* on either side of the grate. *VV* are working doors, through which tools can be introduced to loosen or stir the ore, and cause it to descend uniformly. Such a furnace will roast 1·5 tons of ore in 24 hours.

At the works at Oker, five such kilns, communicating with each other underneath the vault, form a block. The floor is saddle-shaped. The air supply is regulated as in pyrites burners. The construction of the older form of kilns is shown in Figs. 25 and 26.

S is the shaft, *O* the saddle-shaped floor, *Z* the openings for discharging burnt ore, *P* and *V* the working doors, *M* the opening through which the gases pass into the main flue *W*. The raw ores are charged through the top row of working doors *P*. As in the

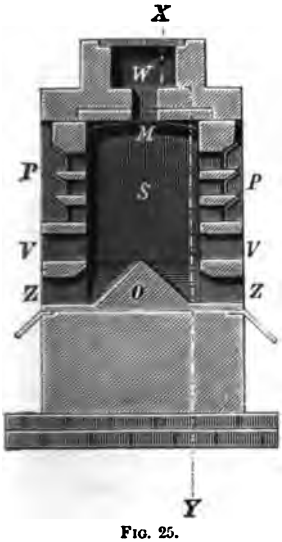


Fig. 25.

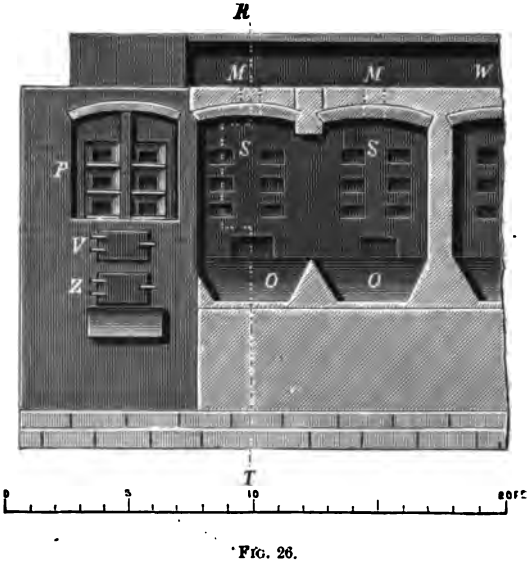


Fig. 26.

pyrites burners, there are recesses in the walls, in which nitric acid is generated.

These furnaces, in which the ore stands at a height of 4 feet 3 inches above the ridge of the floor, can put through 4½ to 5 tons per 24 hours in the block of 5 kilns, or about 1 ton per kiln.

The newer kilns are about 13 feet high, 4 feet wide, and 7 feet 6 inches long. The ore is charged through the roof, as in the Freiberg kilns. Each kiln puts through from 1·4 to 2 tons per 24 hours, according to the character of the ore. From 7 to 10 per cent. of sulphur, corresponding to the percentage of copper, is left in the calcined ore. With ores containing lead, *e.g.*, the so-called *mixed ores* (containing 28 per cent. zinc blende, 25 per cent. pyrites, 15 per cent. chalcopyrite, 11 per cent. galena, 14 per cent. barytes, and 7 per cent. of other gangue), of which 1·8 to 2 tons can be treated in

24 hours, it is not possible to bring the sulphur down low enough to suit the copper contents; it can only be brought down to 10 to 12 per cent., whilst to get a proper matte only some 6 to 7 per cent. of sulphur should be left in the ore. The kiln roasting has therefore with these ores to be followed by a heap roasting.

THE ROASTING OF ORE-FINES IN SHAFT FURNACES

Pulverulent ores cannot be roasted in that form in the kilns just described, because they would pack too close and thus extinguish the fire. It is only in exceptional cases, *e.g.*, at Freiberg, that fines are made into lumps by means of dilute sulphuric acid, or a mother liquor of green vitriol and clay, and these lumps roasted in kilns; this process can only be applied where wages are low and the proportion of fines very small.

As a rule, fine ore, whether got as such in the mine, or in the course of dressing operations, or intentionally produced by crushing lump ore, is roasted in specially designed shaft furnaces, in which the interior is not left open. It is filled with horizontal or inclined plates or prisms, which prevent in part or wholly the free fall of the ore. The shaft has vertical walls, and is square, oblong or circular in cross section.

Most of these furnaces afford the advantage of a thorough calcination, but the disadvantages of the formation of flue-dust, of having but small capacity, and, in the case of lump ore, of the necessity of previously crushing the latter. They are also unsuitable for the calcination of ores poor in sulphur, and that frit or fuse readily.

The gases produced are generally employed in sulphuric acid manufacture; nevertheless such furnaces have been employed in countries where fuel is very dear and labour cheap, for the roasting of ore-fines when no sulphuric acid was to be produced (*e.g.* Gerstenhöfer furnaces for pyritic copper-ore fines at Kedabeg in Transcaucasia). In the furnaces in question, the free fall of the ore may be partly prevented by the obstacles inserted in the shaft, as in the furnaces of Gerstenhöfer and Hasenclever-Helbig, or it may be entirely prevented as in the shelf furnaces. In these the ores rest on a series of horizontal shelves one above the other, and either remain on the same shelf throughout the entire operation (Ollivier and Perret furnace) or they are periodically passed from shelf to shelf by hand (Malétra furnace), or by mechanical means (Spence and MacDougall furnaces) and leave the bottom shelf in a roasted condition.

Gerstenhöfer furnace.—The construction of this furnace is shown

in Figs. 27 and 28. The principle is that of allowing the fine ore to fall through a heated shaft, and of breaking the fall by interposing a series of horizontal triangular clay prisms. These prisms or carriers are so set that their upper surface is horizontal and that ore dropping from an upper carrier is caught on two others below it. The ore is

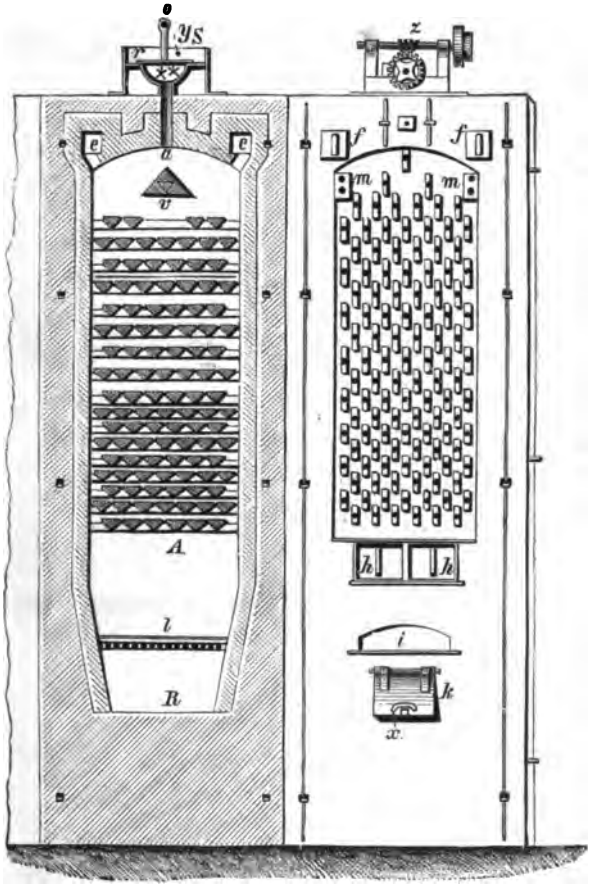


FIG. 27.

continuously charged at the top of the shaft through fluted rolls, and collects upon the upper row of bearers until it has reached its natural angle of repose (33°). It then falls on either side of the carriers and drops upon the prisms of the next lower row, lies there until the angle of repose is again reached, falls on to the next lower row of bearers, and so on until it reaches the floor of the furnace. When

the powder on all the bearers has attained its angle of repose, additional ore cannot lie upon any of the prisms, but falls interrupted by the piles of ore on each bearer, until it gradually reaches the bottom of the furnace. The air required for calcination enters through

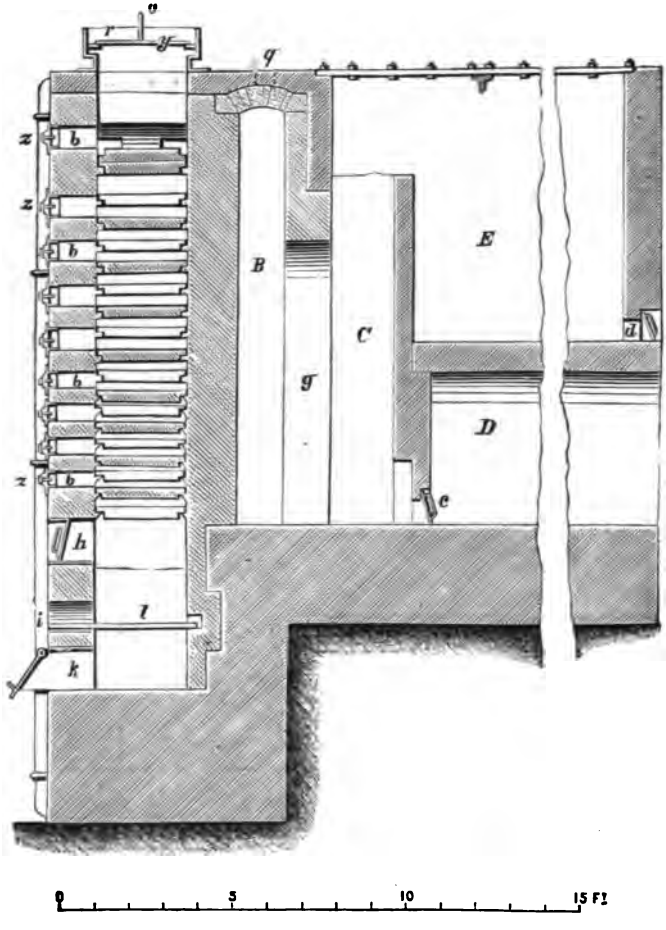


FIG. 28.

lateral openings near the bottom of the furnace and in its upward course comes continually into contact with the particles of falling ore. To start the furnace a temporary grate is put in and firing is continued until the walls of the furnace are red hot. Raw ore is then charged, and firing is still kept up until calcination has commenced

upon every row of bearers, and the ores have reached a red heat. Calcination can then continue by the combustion of the sulphur of the ore without any extraneous fuel, and the temporary grate is withdrawn. The gases produced escape at the top of the furnace and are first led into dust-chambers, in which the flue-dust that is carried up, is allowed to settle; thence they pass to the sulphuric acid chambers. There are openings, closed by cast-iron blocks, in the front wall of the furnace, one opening corresponding to each prism; these serve to observe the progress of the operation, to remove any fritted masses from the prisms, and to keep the interspaces between the prisms clear. In each cast-iron block there is a round peephole which is kept closed by a clay plug.

The height of the shaft varies between 11 feet 6 inches and 16 feet 6 inches, its width between 4 feet 3 inches and 5 feet, and its depth is about 2 feet 8 inches, inside measurements. There are fifteen to seventeen rows of prisms, there being alternately six and seven in a row.

In the above figures, *A* is the shaft, *y* the charging apparatus, which consists of two fluted rolls placed above a slot *a* and driven by a worm wheel and tangent screw. (In many furnaces, there are three slots, three pairs of rolls and three distributors in each furnace.) Below the charging slot *a* there is a distributor *v*. The ore is delivered into a box *r*, the bottom of which forms a sieve that retains any coarse pieces, whilst the fine grains fall through on to the feeding rolls and thus to the distributor. Air enters through the openings *h* and *i*, *e* is the gas outlet, B and C are dust-flues, E is the dust-chamber. D is an archway for cleaning out C. The burnt ore is drawn out through *k*; *l* is the temporary grate, *bb* are the openings for cleaning the prisms, *z* the iron block for closing them.

According to the nature of the ores and the degree of calcination required, a Gerstenhöfer furnace will treat from 2 to 5 tons in 24 hours. The roasting can be regulated to some extent by mixing more or less roasted ore with the raw ore. It is only possible to put through as much as 5 tons when the ore is in coarse grains and the calcination somewhat imperfect.

In spite of its comparatively large output, the Gerstenhöfer furnace has the great disadvantages of making considerable flue-dust and of roasting imperfectly. It is therefore not very largely employed for calcining copper ores, and cannot be recommended where a thorough roast is required, as ores rich in sulphur and poor in copper, like cupriferous pyrites, would give a matte too low in copper after calcination in this furnace.

Hasenclever and Helbig furnace.—The principle of this furnace depends on heating the ore-fines by the simultaneous calcination of lump ore. It consists of a combination of a pyrites burner with a shaft, the latter being furnished with a series of shelves alternately parallel to each other, inclined at an angle of 38°. The fine ore is charged at the top of the furnace, slides slowly down the shelves, because its angle of repose is 33°, and is ultimately removed from the bottom shelf by means of a small roller. The gases produced in the pyrites burner pass first under, then over each of the shelves, being conducted upwards by small flues in the narrow side walls of the shaft; they mix with the gases evolved in the shaft from the burning fine ore, and are led by a flue near the top of the shaft to the sulphuric acid chambers. Figs. 29 and 30 show this furnace. *S* is the shaft connected with the pyrites burners *z*; *p* are the shelves down which the ore slides, *w w'* and *v v'* the flues through which the gases ascend in the directions shown by the arrows. The ore is charged at *a* and is delivered at *o* by the roll *y*. The gases pass to the lead chambers through the flue *r*. In 24 hours 0·5 to 0·8 ton of pyritic fines can be roasted in the shaft, down to 4 to 7 per cent. of sulphur.

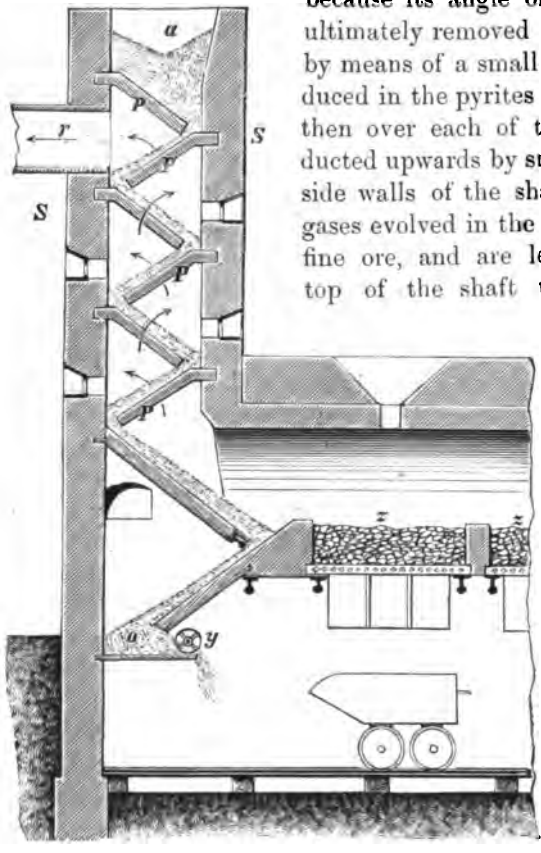


Fig. 29.

These furnaces have the advantage that ores in grains up to 0·6 inch in diameter can be roasted in them, but the serious disadvantage that the roasting of the fines depends on that of the lump ore, so that fine ore in excess of a certain ratio cannot be treated in this furnace. On this account it has been displaced by furnaces in

which the fine ore is roasted independently of the lump ore, and is probably nowhere in use at the present day.

Ollivier and Perret furnace.—This furnace, like the last, depends upon the principle of heating pulverulent ores by means of the hot gases evolved in roasting lump ore, and consists of a combination of a pyrites burner with a shelf furnace. The latter consists of a shaft, into which the pyrites burner is continued, and which contains a series of horizontal shelves, made of fireclay, set about 1 foot apart, and so disposed that the heated gases from the pyrites burner can pass below and above each shelf. The ore to be roasted is spread in a layer 2 inches deep on each shelf and left until the calcination is finished. The hot gases from the pyrites burner ascend through flues in the side walls, heat the shelves and the ore upon them, and mix with the gases evolved from the latter, being ultimately delivered from the upper part of the furnace to the sulphuric acid chambers. The roasted ore is discharged into a vertical chamber in front of the shelves, which is kept filled with roasted ore, which seals the front of the furnace whilst the operation is in progress. Accordingly, in this furnace the ore does not pass from above downwards, but remains stationary on the shelves during calcination.

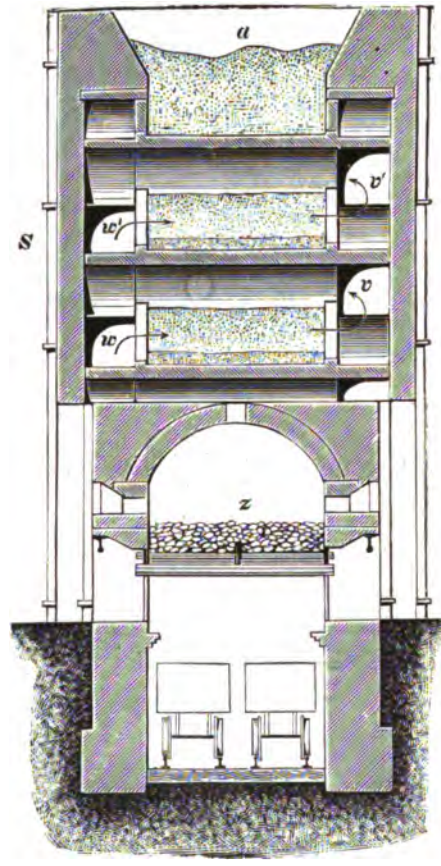


FIG. 30.

Figs. 31 and 32 show the construction of the furnace. *K K* are the pyrites burners, *S S* the shafts provided with the clay shelves *t*; *o o* are openings fitted with iron doors, through which the ore is charged

on to the shelves; *y y* are the flues through which the gases ascend, and *w w* those through which they pass to the sulphuric acid cham-

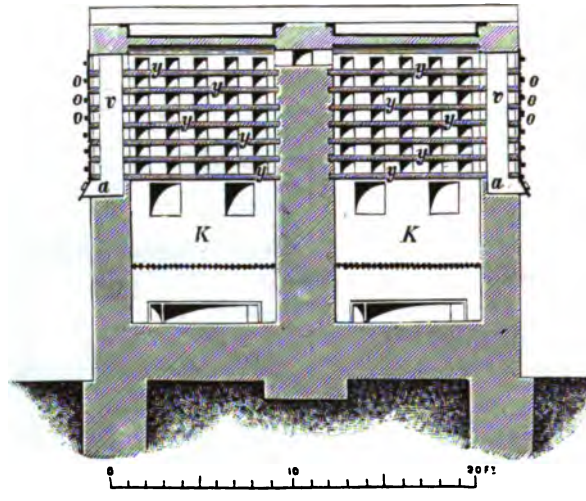


Fig. 31.

bers; *v v* are the vertical chambers to receive the roasted ore, and *a a* the doors through which it is discharged from the furnace.

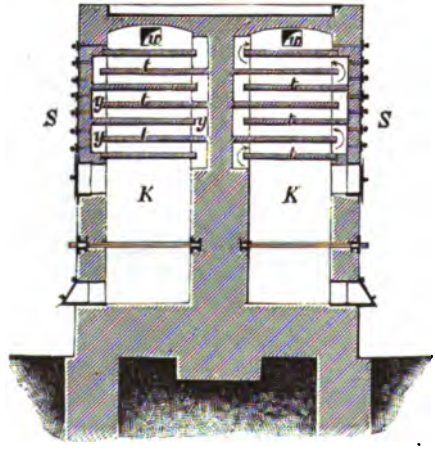


Fig. 32.

This furnace roasts well but has the same objection as the Hasenclever-Helbig furnace, namely, that the calcination of the fines depends upon the ratio of the latter to the lump ore, which must be 1 : 1, or at the outside 2 : 1. For this reason it has, like the last-named furnace, been displaced by independent furnaces for roasting fines. According to Lunge, it is still in use in some French sulphuric acid works.

Malétra furnace.—This is the best furnace for the calcination of cupriferous pyrites, not only because it admits of a very perfect roasting (down to 1 per cent. of sulphur), but also because it will treat ore in coarse grains. It was designed by Juhel, the manager of

the sulphuric acid works of Malétra in Rouen, and relies upon the possibility of roasting pulverulent ores in a shaft furnace provided with shelves even without the application of extraneous heat, as in the two last-named furnaces. The furnace is simply a vertical shaft with no pyrites burner, provided with horizontal shelves of fire-clay. The shelves are placed at a certain distance apart, so that the ore can be charged on to the top shelf, be made to pass from shelf to shelf, and finally be withdrawn completely roasted from the bottom shelf. To start the furnace, it is heated to redness by means of extraneous fuel, and then charged with ore-fines; the calcination thus set up continues of itself, the heat evolved being sufficient to maintain the temperature. A working door is supplied to each shelf.

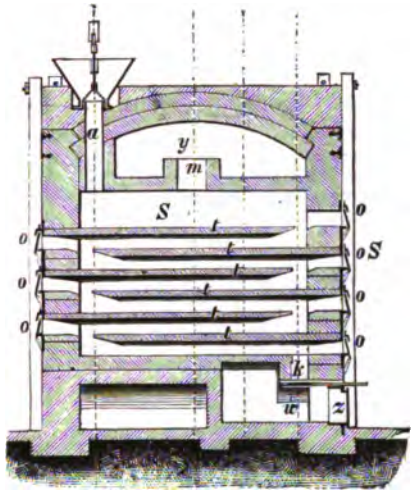


FIG. 83.

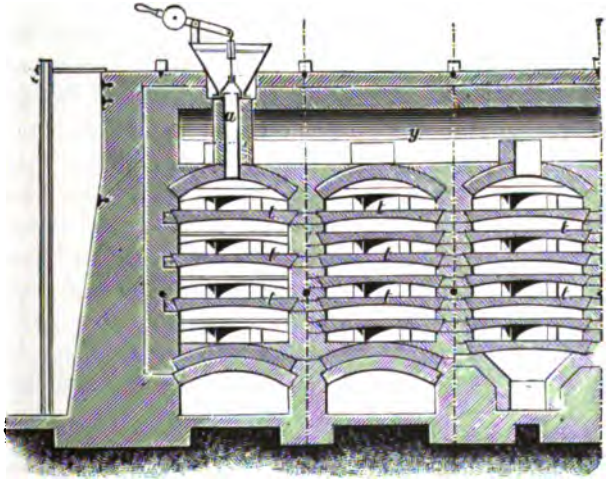


FIG. 84.

An improved form of this furnace, modified by Schaffner of Aussig, is being used at Aussig for roasting cupriferous pyrites, and is shown

in Figs. 33 to 37. *S* is the shaft, *t t* the clay shelves; *a* is a vertical flue for charging the small ore on to the topmost shelf by means of a

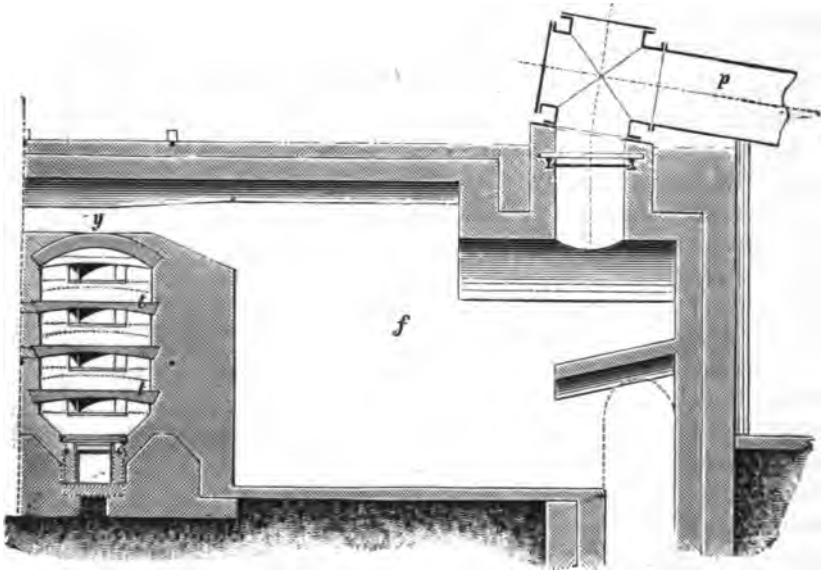


FIG. 35.

hopper; *o o* are the working doors, the planed edges of which are arranged to slide in planed grooves in ribs cast on to the front plates of the furnace. These doors are opened when the ore has to be rabbled, or transferred from one shelf to the next. The roasted ore drops through the vertical flue *k* into the chamber *w*, whence it is drawn out through the door *z*. The gases evolved pass through an opening *m* in the roof into a flue *y*, which is common to a row of these furnaces, thence into the dust-chamber *f*, and finally through the flue *p* to the lead-chambers.

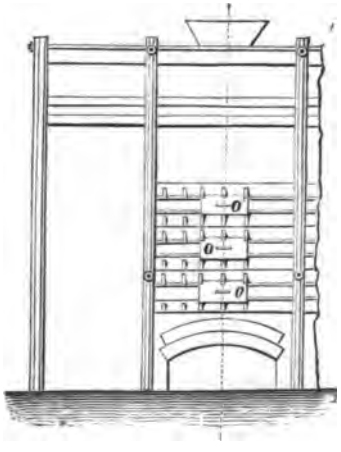


FIG. 36.

Each Malétra furnace (each shaft) is capable of roasting $\frac{3}{4}$ ton of fine and granulated ore in twenty-four hours down to 1 to 2 per cent. of sulphur. A block of four furnaces will treat 3 tons of ore smalls in twenty-four hours.

A furnace described by Jurisch,[1] which is employed in France, and which is said to have given the best results of any form of Malétra furnace in a series of comparative tests, is shown in Figs. 38 and 39. Here the shelves are flat above and below, and are supported in the centre; they are 2·5 inches thick, 28 inches long, and 26 inches broad, are cut square on their longer sides, but are half-checked along the shorter, and are joined together as shown in Fig. 40. The gases from a pair of furnaces enter the wide flue *z* which serves as a dust-chamber, and thence pass into the flue *y*.

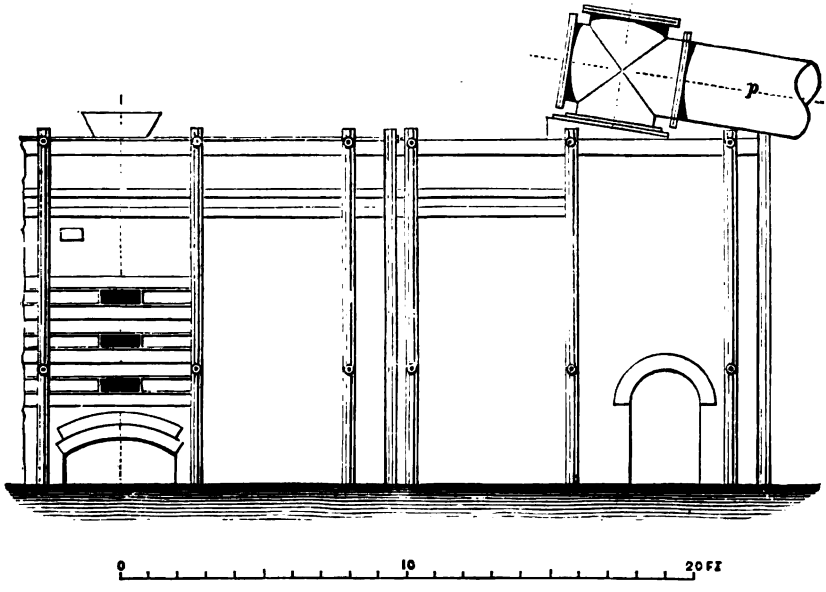


FIG. 37.

The walls of the flue *z* form the back walls of a row of furnaces on either side. This arrangement is preferable to the older form adopted by Schaffner, because the back walls of the furnace when freely exposed to the air were found to be very sensitive to air currents, and admitted too much air into the furnace. Each shelf of this furnace possesses 35 square feet of heating surface, each furnace has 210 square feet. On each square foot of surface 6½ lbs. of pyrites can be roasted in twenty-four hours.

The Malétra furnace is the best furnace for ores rich in sulphur, and that are not apt to sinter.

[1] *Handbuch der Schwefelsäure-Fabrication*, Stuttgart, 1893.

Spence furnace.—This is a Malétra furnace, in which the charging of the ore, its transfer from shelf to shelf, and its discharge are performed automatically. It is used in countries where wages are high and especially in the United States, for the calcination of cupriferous pyrites. Its principle is shown in Figs. 41 and 42. The shelves *p* fill the entire cross section of the furnace, but are slotted, so that the ore can drop from each shelf to the one below. On each shelf there is a rabble *r*, whose handle *s*, 16 to 20 feet in length, is attached to a vertical rod *m* carried on wheels; the latter is periodically moved backwards or forwards by water or steam power, this motion being

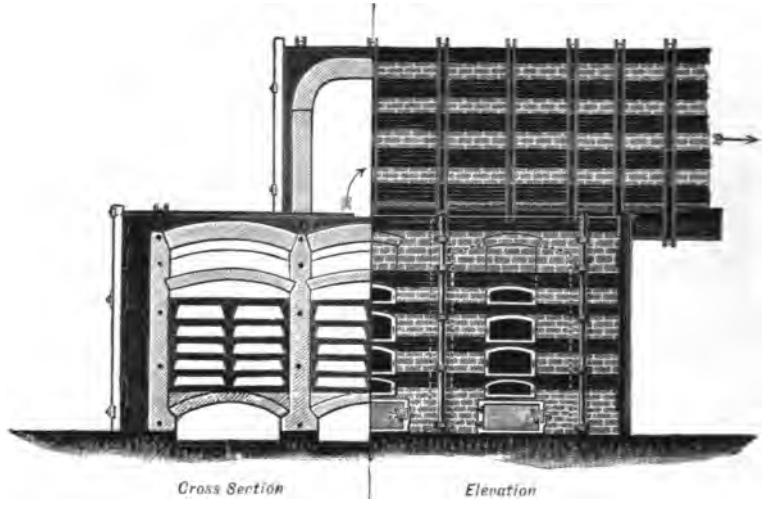


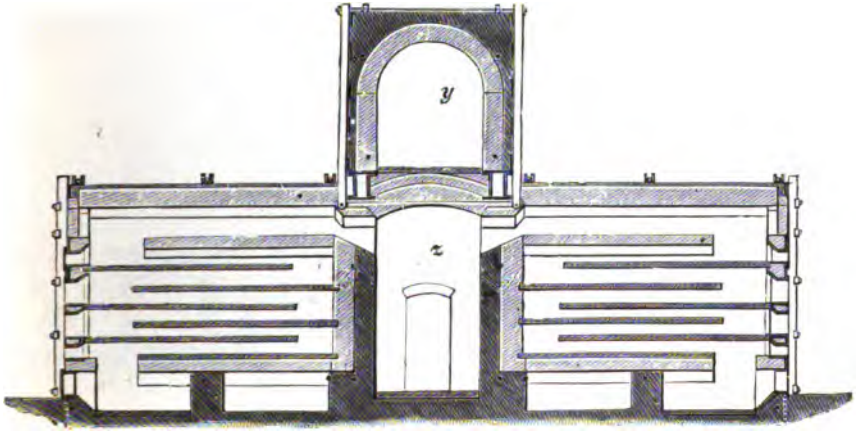
FIG. 38.

communicated to the rabble inside the oven. The ore is charged by means of a hopper *T* furnished with a slide, which is also attached to the rod *m* and allows a small quantity of ore to drop into the furnace each time it is drawn back. The ore is thus slowly pushed across the shelves *p*, and is at last discharged in the roasted state into the waggon *w*. Each furnace has four, or more recently five, shelves whose vertical distance apart is about 14 inches. The furnace is about 16 to 20 feet long by 34 feet wide.

The author has seen this furnace in operation at the Parrot Works, Montana, where 5 tons of pyritic copper ores, containing 35 per cent. of sulphur, were being calcined in each furnace in 24 hours. The roasting can be completed down to 1 per cent. of sulphur. The iron rabbles and rods are kept covered with ore, as their life is thereby

greatly prolonged; it is said to be about two years. But little labour is required, as two workmen can attend to six double furnaces.

An improved Spence furnace[1] has been designed and built by Messrs. Keller, Gaylord and Cole at the Parrot Company's Works at Butte. Each furnace consists of a pair of blocks of six hearths each, the machinery for driving the rabbles lying between the two. Each double block is 39 feet long, 22 feet 6 inches wide, and 24 feet 9 inches high. The rabbling arrangement consists of six sets of arms



Longitudinal Section

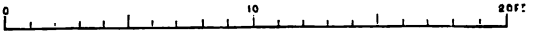


FIG. 39.

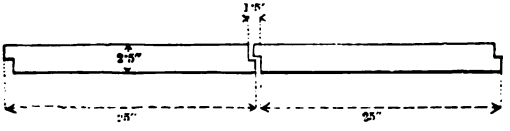


FIG. 40.

on each side, passing through slots into their respective hearths. These arms receive a back and forwards motion by means of a steel wire rope passing round a driving wheel which is turned alternately in opposite directions by means of a pinion gearing with a rack attached to a hydraulic piston. The slots are closed by steel tapes that also receive a reciprocating motion by means of pulleys at either end of their travel, worked by springs and weights. Each rabbling arm has two sets of plough blades, lying in the same plane, but so

[1] The description of this furnace is abstracted from E. D. Peters's *Modern Copper Smelting*, seventh edition, p. 214.—[H. L.]

arranged that the blades on one side of the arm alternate with those on the other. Each time that the motion of the rabbling arm is reversed it is turned through 90°, so that the plough blades always

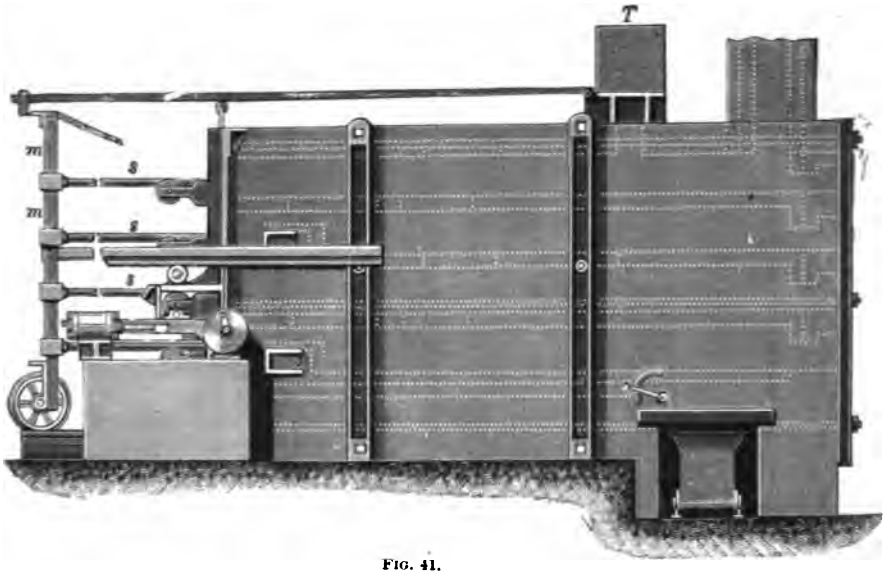


FIG. 41.

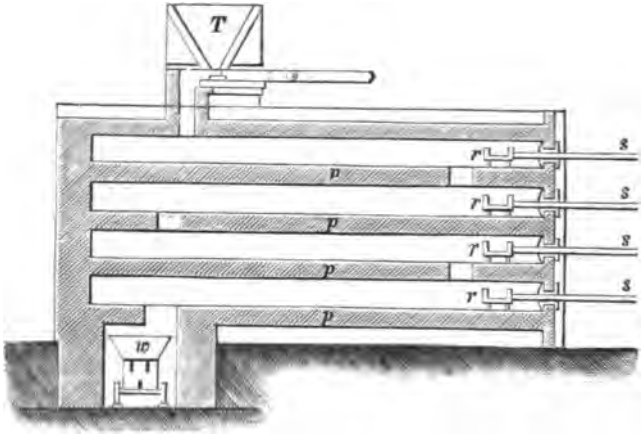


FIG. 42.

traverse the ore in one direction only, and lie horizontally above the ore without touching it on the return journey. Each set of plough blades is thus brought into play once in four strokes, and as the blades alternate, the ridges of one stroke correspond to the furrows of the next; the plough blades have thus ample time to cool off.

Each block of six hearths is provided with a fireplace 2 feet 6 inches by 4 feet, fired with slack, the coal containing about 18 per cent. of ash. This furnace (the double block) will roast 45 (short) tons of concentrates with 41 per cent. of sulphur down to between 7 and 10 per cent. of sulphur, in 24 hours with the consumption of $\frac{3}{4}$ ton of coal slack. The ore is fed automatically by means of fluted rollers at the top of the furnace, and one man, working a 12 hours shift, is able to do all the necessary work including firing, for three sets of these furnaces, so that the labour cost is very low. The rabble arms and ploughs are the only part of the rabbling mechanism exposed to heat, and the life of these pieces is said to average some four months. About two horse-power are required to drive the machinery. The results obtained with this furnace are spoken of as highly satisfactory.

MacDougall furnace.—Like the last, this is a shelf furnace in which the ore is advanced automatically. The furnace body is cylindrical and the shelves are circular with openings alternately at the centre and the circumference to permit of the descent of the ore. A vertical shaft traverses the centre of the furnace, carrying rabbles corresponding to the shelves. The air required for combustion is forced in at the bottom by a fan; the ore to be roasted is delivered on to the top shelf by means of a bucket elevator, and by the motion of the rabbles it is gradually dropped from shelf to shelf, falling alternately at the centre and at the circumference, till it reaches the floor of the furnace in a roasted state. The gases escape at the top of the furnace through a flue leading to the acid chambers. The original MacDougall furnace is shown in Figs. 43 and 44 after Lunge,[1] as it was used at Liverpool, where it has however been given up on account of making too much flue-dust. It consists of a cast-iron cylinder 11 feet 6 inches high and 6 feet in diameter, made up of seven rings bolted together. Inside it are the flat arches g to g_5 made of firebrick. These are traversed by the central shaft w, 6 inches in diameter, carrying the arms k to k_6 furnished with rabbles. There are apertures alternately at the centre (d) and at the circumference (p) of each arch, the former being 14·6 inches in diameter. The under side of the arms is furnished with tines turned towards the centre on such of the arches as are provided with central discharge, and towards the circumference on the others. As the shaft revolves the ore is accordingly forced through the central and peripheral openings alternately until it ultimately reaches the furnace bottom, where it is pushed into the tube x, which is kept closed by the sliding door u.

[1] *Handbuch der Soda-Industrie I.*, Braunschweig, 1893.

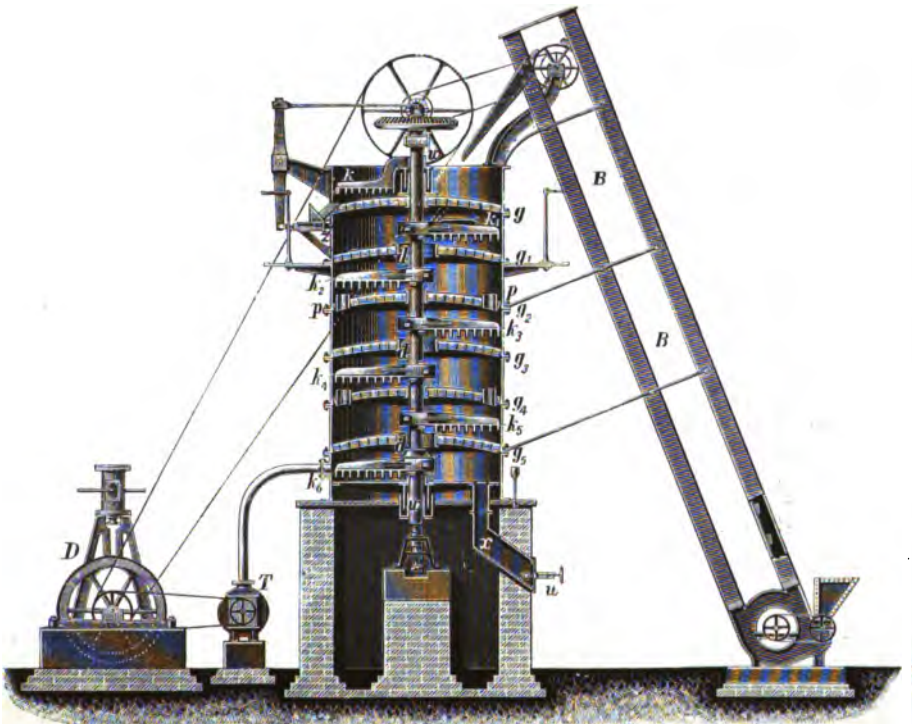


Fig. 43.

Fig. 44.

The ore is lifted by the bucket elevator B to the top of the furnace and delivered on the arch g; the rabble k forces it through an opening outside the furnace, whence the piston z pushes it onto the arch g_1 where its descent through the furnace commences. T is a fan supplying air to the furnace; it is driven together with the vertical shaft w and the elevator B by an engine at D; the gases escape through the flue N. There are manholes at O through which repairs can be executed. Such a furnace roasts 3½ tons of concentrates in 24 hours; the engine consumes 4 tons of fuel per week.

This furnace does good work when the air is supplied in a steady stream, and when due provision is made for collecting the flue-dust that is carried off. It admits of good roasting, with a considerable saving in wages, but the ironwork requires repair and renewal from time to time. The author saw a furnace on this principle, square in cross section with three partitions, in 1892 at the Nicholson Works near Brooklyn, used for calcining cupriferous pyrites with 5 per cent. of copper from Canada. A furnace there calcines 3 to 3½ tons of ore in 24 hours down to 3 per cent. of sulphur.

CALCINATION IN REVERBERATORY FURNACES

Reverberatory furnaces should be employed for roasting sulphuretted copper ores, when the sulphur is not required to be utilised in sulphuric acid manufacture and when the extraction of the copper from the ore is to be performed rapidly. They are suitable for all kinds of copper ores. Ores rich in copper and poor in sulphur should not as a rule be calcined, but be smelted raw for matte; this also applies to ores containing but small amounts of metallic sulphides. Cupriferous pyrites can be roasted with the least amount of fuel, and in the shortest time in the reverberatory furnace, because the sulphur in them takes the place of a portion of the fuel.

Ores to be roasted in reverberatories must first be crushed unless they are already in the form of concentrates or fines. The size of grain best adapted to calcination must be determined experimentally in each individual case.

For thorough calcination, the ore in the furnace must be brought into the most intimate contact possible with the air current; with this object it is rabbled by hand or by machinery. The working chamber or hearth of reverberatory furnaces is either fixed or is movable either wholly or in part. We may therefore distinguish:

1. Fixed reverberatory furnaces { with hand rabbling. / with machine rabbling.

2. Reverberatory furnaces with movable beds.

3. Reverberatory furnaces with movable (rotating cylindrical) working chambers.

Well constructed reverberatory furnaces with fixed hearths and handworking give favourable results where labour is cheap. When wages are high, this form of furnace is economically inferior to furnaces with fixed hearths and machine rabbling, or to revolving cylinders.

CALCINATION IN FIXED HEARTHS WORKED BY HAND

The only furnaces that need be considered under this head for the roasting of copper ores are those with a long hearth worked continuously (*Fortschaufelungsöfen*). In these the ore is charged at the point furthest removed from the firebridge, and is moved at stated times in stated quantities towards the hottest part of the furnace till it is drawn off, completely roasted, at the firebridge. The older type of smaller furnace, worked discontinuously, in which the whole of the ore to be roasted was charged at one time, and drawn out at one time when the calcination was complete, has gone out of use everywhere on account of its high cost both in fuel and in labour, and need not, therefore, be described here.

The normal type of furnace is that with one hearth and working doors on either side. Separate hearths situated one above the other present great difficulties in working the upper hearths, and should only be employed under exceptional circumstances, such as very dear land or want of space.

The size of the hearth must depend upon the percentage of sulphur in the charge; the higher the latter, the longer can the hearths be, as they are heated by the combustion of the sulphur. Experience has shown that a length of 66 feet is about the maximum, as a greater length gives no better results as regards calcination, whilst it increases both the first cost and the expense of labour. The above length can be used for ores that are richest in sulphur down to those containing about 25 per cent., or with pyrites even down to 20 per cent. of sulphur. With ores carrying 20 per cent. of sulphur as monosulphide, a hearth of 50 feet is long enough, and with 15 per cent. of sulphur its length should be from 33 to 40 feet. The width of the hearth should be such that the ore can be conveniently rabbled and moved forwards, the efficiency of the furnace increasing the wider the hearth is within this limit. On the continent of Europe the width varies from 8 feet to 11 feet 6 inches, whilst in America hearths up to 16 feet wide inside have been used with good results.

As the ores can still be thoroughly worked and roasted with the latter width, it must be looked upon as the most suitable for the calcination of sulphuretted copper ores. The number of working

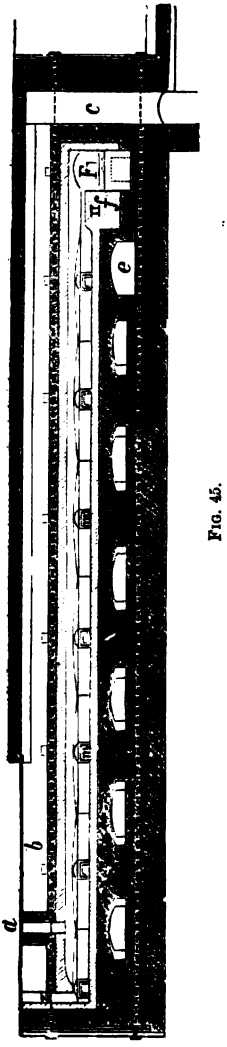


FIG. 45.

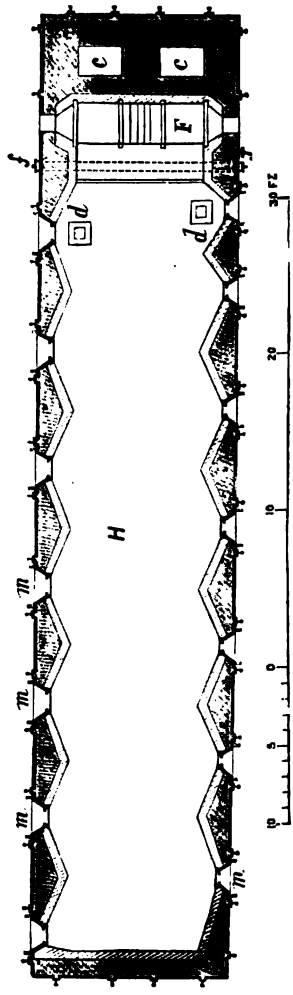


FIG. 46.

doors on either side must be limited as far as possible, as they tend to cool the furnace down. Experience has shown that the distance between the centre lines of neighbouring doors should not exceed 8 feet, nor be less than 6 feet. The brickwork projections between the doors should be kept as flat as possible. In order to utilise

the heat as completely as possible, it is well to give the arch of the furnace a gentle slope down towards the flue end, or else the bed may rise gently upwards, either continuously or in several steps.

Figs. 45 to 47 show the arrangement of such a roasting furnace. *E* is the working chamber (the term hearth is applied indifferently to this as well as to the bed or hearth proper), *f* the hollow, air-cooled fire-bridge, *F* the fireplace, *H* the hearth or bed. The ores are charged through the opening *a*, near the flue, which can be closed when not in use, and they are gradually advanced towards the fire-

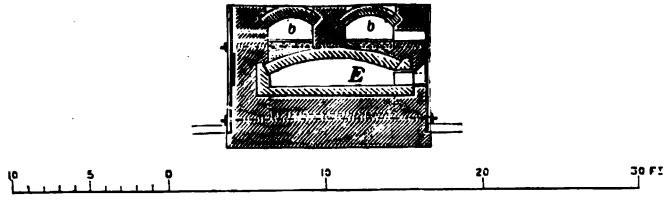


FIG. 47.

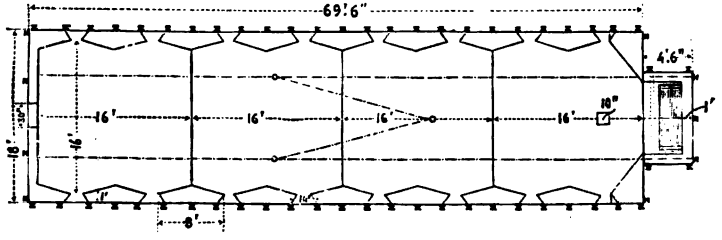


FIG. 48.

bridge, where they are emptied through vertical tubes *d* into a space below the hearth. The working doors are shown at *m m*. The products of combustion traverse the full length of the hearth and escape through the flue *z*, into two flues *b b* running along over the top of the arch, whence they pass by the flues *c c* to the stack. In proportion as calcined ore is removed from the hearth, the portions of the charge lying in front of each working door are advanced and a fresh charge is dropped in front of the first pair of working doors.

The construction of a modern calciner such as is used in the United States, with stepped hearth 16 feet wide and 64 feet long, is shown in Figs. 48 to 50.

The quantity of ore that such a furnace is able to roast depends upon its capacity and upon the richness of the ore in sulphur.

Pyritic ores rich in sulphur roast more rapidly than ores low in sulphur.

In the large American calciner, shown above, some twelve tons of ore rich in sulphur can be roasted in twenty-four hours, with a consumption of one ton of coal or two cords of soft wood, and with the labour of four men, two men on each twelve hours shift, together with one quarter of a man's time on a six hour shift, for transporting the ore and filling it into the hopper. The total amount of ore in the furnace at one time is eight tons, or two tons to each

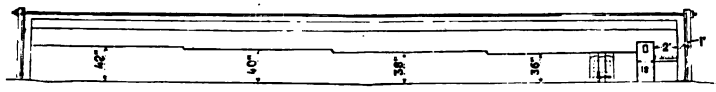


FIG. 49.

step hearth; one fourth of the total charge is removed every four hours, so that a charge of ore remains sixteen hours in the furnace. At the Parrot works, Butte, Montana, whilst the author was there, ten tons of ore containing 35 per cent. of sulphur were roasted down to 7 per cent. in one of these calciners in twenty-four hours, with two men on each twelve hours shift, and with the consumption of two and a quarter cords of wood.

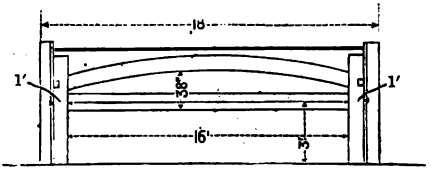


FIG. 50.

At the works at Oker, a furnace, 52 feet 6 inches long and 11 feet wide, calcined four tons of copper ore from 20 per cent. down to 8 per cent. of sulphur with a coal consumption of 30 per cent. of the weight of the ore. Observations on the degree of calcination of various kinds of ore in these furnaces have been recorded by Peters, Talbot and Ames, as shown in the subjoined table:—

No. of test.	Percentage of copper.	Percentage of sulphur.	Loss of weight on roasting. Per cent.	Percentage of copper in roasted ore.				Percentage of sulphur in roasted ore.	Time occupied in hours.	Character of the ore.
				As oxide.	As sulphate.	As sulphide.	Total.			
1	7·6	37	14·5	3·65	3·25	1·65	8·55	6·41	16	Pyritic ore.
2	7·6	39	11·3	2·27	3·10	2·80	8·17	11·30	12	
3	16·4	31	6·4	7·30	3·44	6·80	17·34	8·20	18	Bornite with pyrites and blende.
4	16·4	31	9·5	12·80	2·80	2·10	17·70	4·60	24	

The loss of weight occasioned by the removal of sulphur is in part counterbalanced by the transformation of sulphides into oxides and sulphates.

CALCINATION IN FIXED REVERBERATORY FURNACES BY THE AID OF MACHINERY

Among these furnaces may be cited that of O'Harra improved by Allen-Brown, Pearce's Turret furnace, Brown's Horseshoe furnace, and Parkes's furnace. The Stetefeldt furnace, a reverberatory shaft furnace, into which the ore is mechanically fed, and then falls freely through the shaft, has given excellent results in the chloridising roasting of silver ores, but has not yet been applied to the calcination of copper ores.

The O'Harra furnace has the largest capacity of any reverberatory furnace at present in use, as it can calcine some thirty tons of copper ore in twenty-four hours.

It consists of a reverberatory furnace with two hearths, one above the other, over which rabbles are dragged by means of two endless chains fixed a certain distance apart. These rabbles not only turn the ore over, but drag it slowly forward and discharge it at the bottom of the lower hearth. The wheels round which the endless chains pass are outside the furnace. The rabbles are in the shape of a ploughshare, made of sheet iron, and each set covers one half the width of the hearth. To allow them to pass over both hearths the latter are closed at their ends by means of hinged doors of sheet iron, which open to allow the rabbles to pass and then close again. Firing takes place from fireplaces set along the longer sides of the hearths; in the larger furnaces there are eight, four for each of the upper and lower hearths. The chimney flues are also lateral. Air is admitted through openings at the sides that can be closed as required. In the older form of O'Harra furnace, shown in Fig. 51, the chains ran over the hearths themselves; this arrangement caused rapid destruction of the chains and a correspondingly high working cost, owing to the contact of the chains with, and their friction against, the glowing sulphides. In the modern improved furnaces of Brown-Allen, as built by Fraser and Chalmers, of Chicago, the chains do not pass over the hearth, but in longitudinal channels on either side of it; rails are laid in these channels, upon which run small carriages connected with the chains. These channels have a longitudinal slot in the inner wall that is nearest the hearth; through this slot pass iron bars which are connected with the carriages, and

which carry the plough-like rabbles at their other end, the slot allowing these rabbles to be carried along.

The construction of the O'Harra-Brown-Allen furnace, as seen in

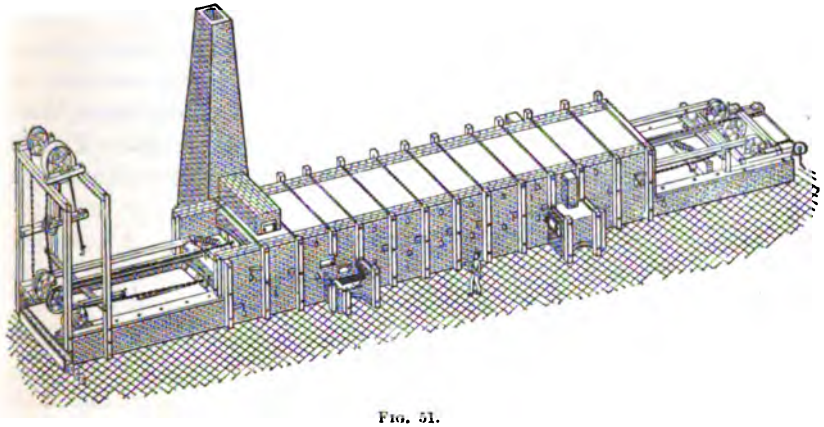


Fig. 51.

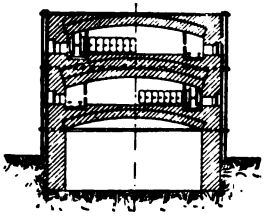


Fig. 52.

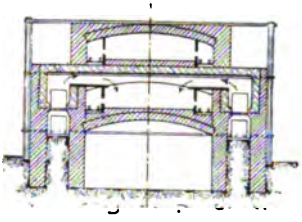


Fig. 53.

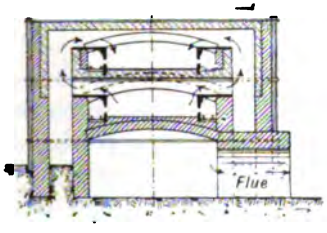


Fig. 54.

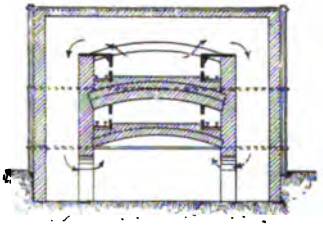


Fig. 55.

operation by the author at Butte, Montana, and at Argo, Colorado, is shown in Figs. 52 to 58. Fig. 52 shows the channels on either side of the hearth, the carriages in them, and the rabbles connected with the carriages. It also shows how the admission of air is provided for by means of openings in the long side walls of the furnace, through

which the air enters the channels and passes, through the slots in these, to the ore upon the hearth.

Fig. 57 shows the path of the ore through the furnace; it is charged automatically at *A* on to the upper hearth, falls at the opposite end of this hearth through a slot on to the lower hearth, and is discharged either through a slot at *B* or through an opening at the end of the lower hearth into a waggon. The fire-places are shown in Figs. 54, 55, 57 and 58. The gases evolved pass downwards from the hearth into a dust-chamber and thence to the stack. Fig. 56 shows an external elevation of the furnace. The Butte and Boston

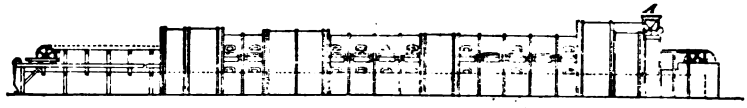


FIG. 56.

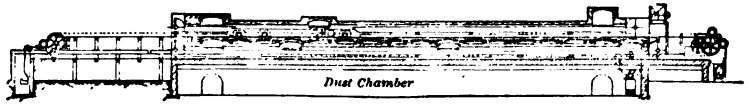


FIG. 57.

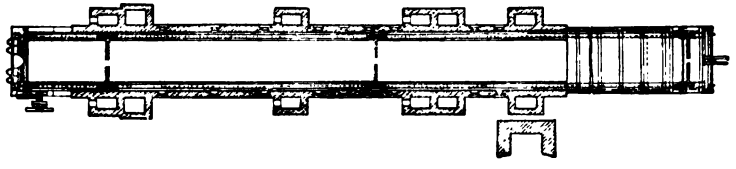


FIG. 58.

Works, Butte, Montana, which had been burnt down just before the author's visit to Montana, had worked eight of these furnaces with satisfactory results. At the Butte and Montana Works, Butte, Montana, which the author also visited, an O'Harra furnace, in which the chains travel on the hearths, having hearths 96 feet long and 16 feet wide in the clear, on which the ore formed a layer 4 inches deep, with four fire-places each for the upper and lower hearths, calcined in twenty-four hours 25 tons of ore from 30 per cent. down to 7 per cent. of sulphur, with a consumption of 2 tons of coals exclusive of that used to generate the power.

At the Argo works in Colorado an O'Harra-Brown-Allen furnace roasts in twenty-four hours 30 tons of ore from 30 per cent. down to

6 per cent. of sulphur, with a consumption of 6 tons of coal; one man can attend to two such furnaces.

The O'Harra furnace is expensive in first cost, but presents the advantages of good calcination, large capacity, and very low cost of labour. Up to the present time it has been used with the greatest success in the United States.

Pearce's Turret furnace [1] has been used with the best results in the United States. The general arrangement is shown in Fig. 15*a*. It is distinguished from the O'Harra-Brown furnace by possessing only one ring-shaped hearth, whilst the movable rabbles are connected by arms with a revolving vertical shaft, which is situated in the centre of the free space surrounded by the ring-shaped hearth, and which is driven by steam power. The fire-places are situated on the outer circumference of the furnace; the flue is in the arch above the ring-shaped hearth. The roasted ore is discharged through a

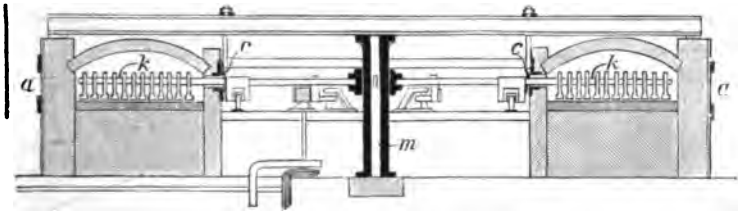


FIG. 15*a*.[2]

slot in the bed of the hearth. In the section, m is the vertical shaft to which the rabble arms are secured that carry the ploughblades k; these arms consist of hollow iron pipes, through which air is injected into the furnace for the purpose of aiding the calcination and at the same time keeping the arms cool. The slot in the inner wall of the furnace, through which the rabble arms project into the hearth, is shown at c; this slot is kept closed by a steel band attached to the rabble arms and revolving with them. This furnace is cheaper to construct than the O'Harra furnace. It requires about two horse-power to drive it, and one man can attend to three furnaces. Its capacity is from 13 to 16 tons in twenty-four hours, according to the nature of the ore. At Argo, Colorado,[3] 16 tons of pyritic ore were roasted in twenty-four hours from 36 per cent. down to 4·75 per cent. of sulphur, with a fuel

[1] Imp. German Patent, No. 70,807, December 1892.

[2] The Figs. 15*a* to 22*a*, with the accompanying descriptions, have been transferred from Vol. ii. of the original. [H. L.]

[3] Peters, *op. cit.* p. 211.

consumption of 18 per cent. of the weight of the ore. The results obtained by this furnace are most highly spoken of.

The Brown Horseshoe furnace is a furnace which in plan occupies a considerable portion of a circle so as to resemble in shape a horseshoe.

Its construction, as built by Messrs. Fraser and Chalmers, of

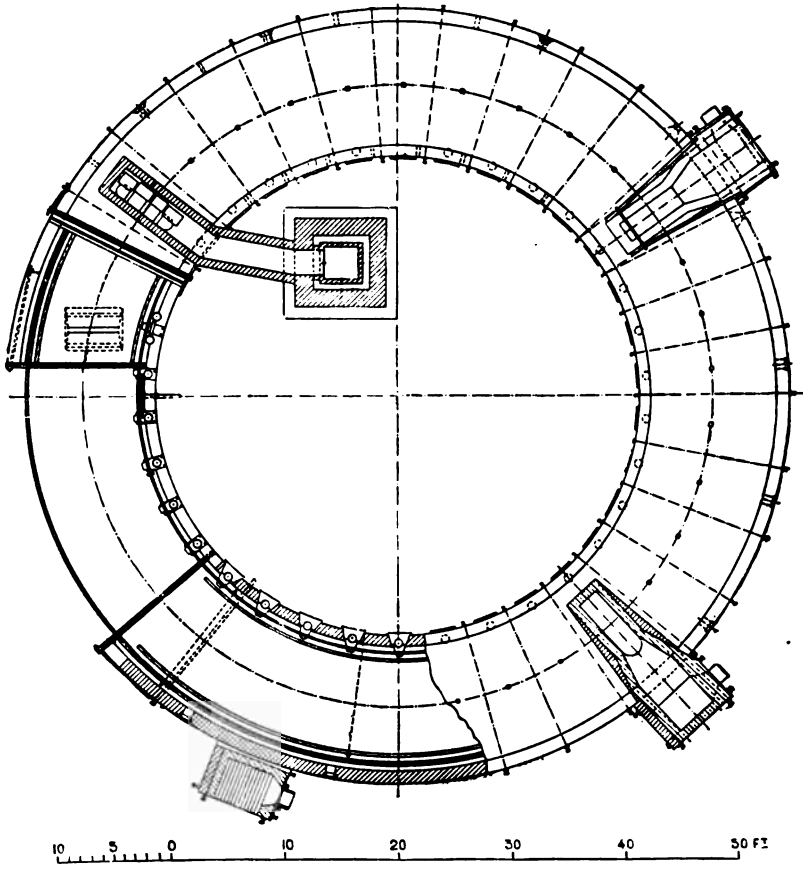


FIG. 16*a*.

Chicago, as shown in Figs. 16*a* to 22*a*. Fig. 16*a* is a ground plan; Fig. 17*a* a vertical section through the furnace proper; Fig. 18*a* a vertical section through the hearth and flue; Fig. 19*a* a vertical section through the flue to the stack; Fig. 20*a* a vertical section through the fire-grate and hearth; Fig. 21*a* a vertical section through the rear end of the furnace where the ore is discharged; and Fig. 22*a* a vertical section through the front or charging end.

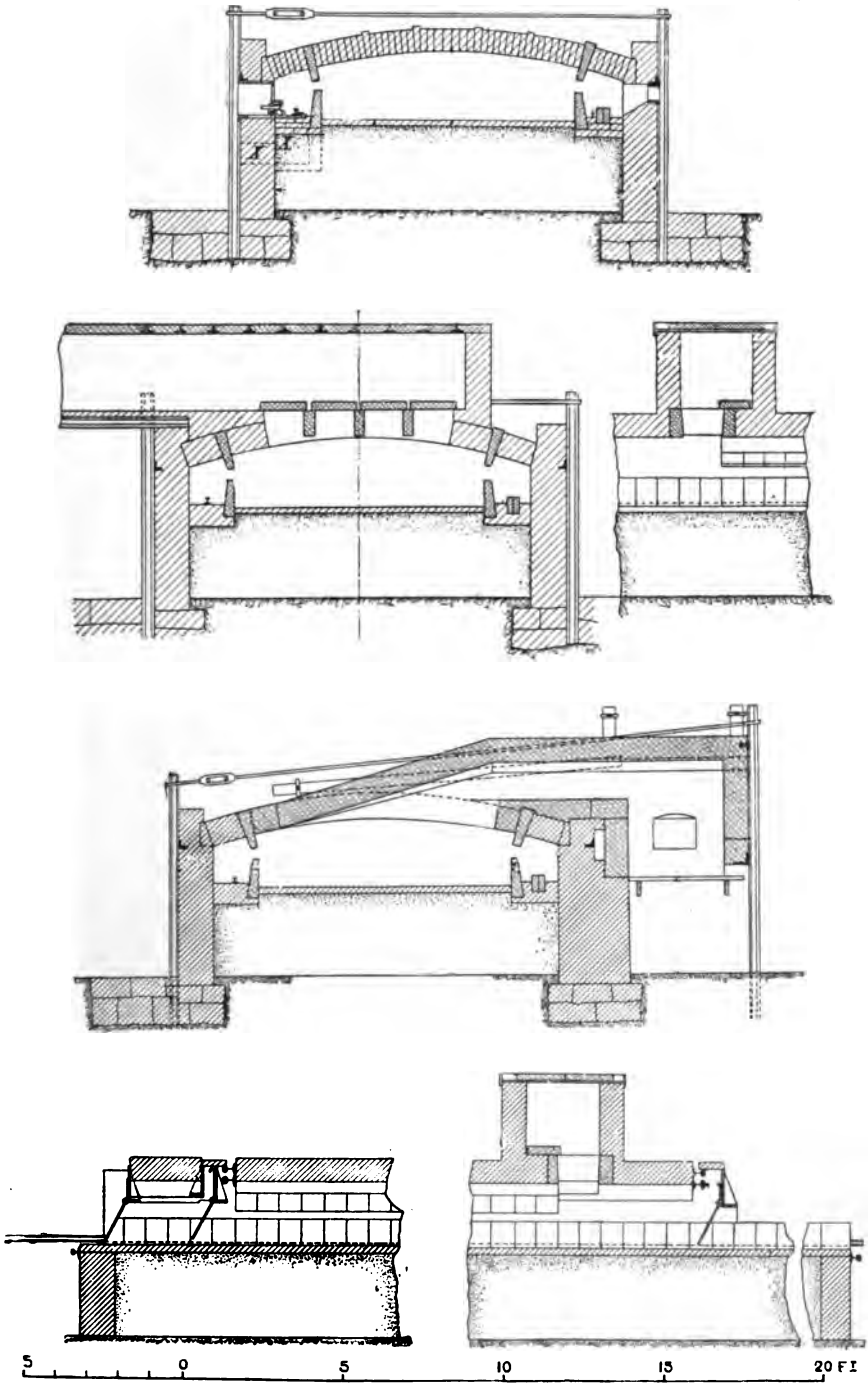


FIG. 17*a*—22*a*.

As is shown by the plan of the furnace, the hearth occupies about four-fifths of the annular space, one-fifth of the latter lying between the two ends of the hearth; this latter space is left free and serves to cool the rabbles passing over it. On either side of the hearth there are annular divisions which are connected with the hearth by a broad slot. In the division nearer to the centre a rail is laid upon which carriages run connected with the rabbles. In the outer division a path of hard firebrick tiles is laid, on which run carriages fitted with broad wheels, and also connected with the rabbles. These carriages, and the rabbles attached to them, are kept in motion by a circular endless wire rope running over guide sheaves and tension pulleys. There are three fire-places situated outside the outer circumference of the hearth; the flames pass through a short horizontal flue, and thence through an aperture in the arch into the hearth itself (Fig. 20*a*). They there unite and traverse the length of the hearth, escaping through several flues close to the charging end of the furnace; these flues lead into a main flue which communicates with the stack situated at the centre of the circle enclosed by the furnace (Figs. 18*a*, 19*a* and 16*a*).

The ore is charged by an automatic feeder at the fluebridge end of the furnace (Figs. 22*a* and 16*a*). By means of the rabbles, of which there are always two in the furnace at the same time, the ore is gradually carried forward and discharged at the other end of the furnace (Fig. 21*a*). The furnace is closed at either end by pairs of doors of sheet iron hung on hinges which are lifted by the motion of the rabbles and then close automatically. These doors are a short distance apart (Fig. 21*a*), and are so arranged that one closes before the other can be opened, so that the admission of cold air at the extremities of the furnace is prevented. In the outer walls of the furnace there are peepholes at definite distances apart, through which the air required for oxidation can enter the hearth. The power consumption of the furnace is 1½ horse-power, and it is said to roast about 18 tons of ore in twenty-four hours with a fuel consumption of 3½ tons.

More recently Mr. Brown[1] has built his furnace both straight-lined and elliptical in plan.

Parkes's furnace.—This is a reverberatory furnace, with two circular hearths lying one above the other; a vertical iron shaft traverses the furnace, carrying arms to which rabbles are attached, which stir up the ore lying on the hearths when the shaft revolves.

[1] H. P. Brown, "Mechanical Roasting of Ores," *Trans. Fed. Inst. Min. Eng.* vol. xi. p. 369.

Fig. 59 shows the construction of an older form of Parkes's furnace; in it *a* is the lower hearth, 12 feet 6 inches in diameter, *b* the upper hearth, *n* the fireplace, 4 feet square, *o* the firebridge, *m* the vertical shaft, with its rabbles for each hearth; *k k* are the working doors for the respective hearths. The ore can be dropped through a passage from the upper to the lower hearth. The products of combustion

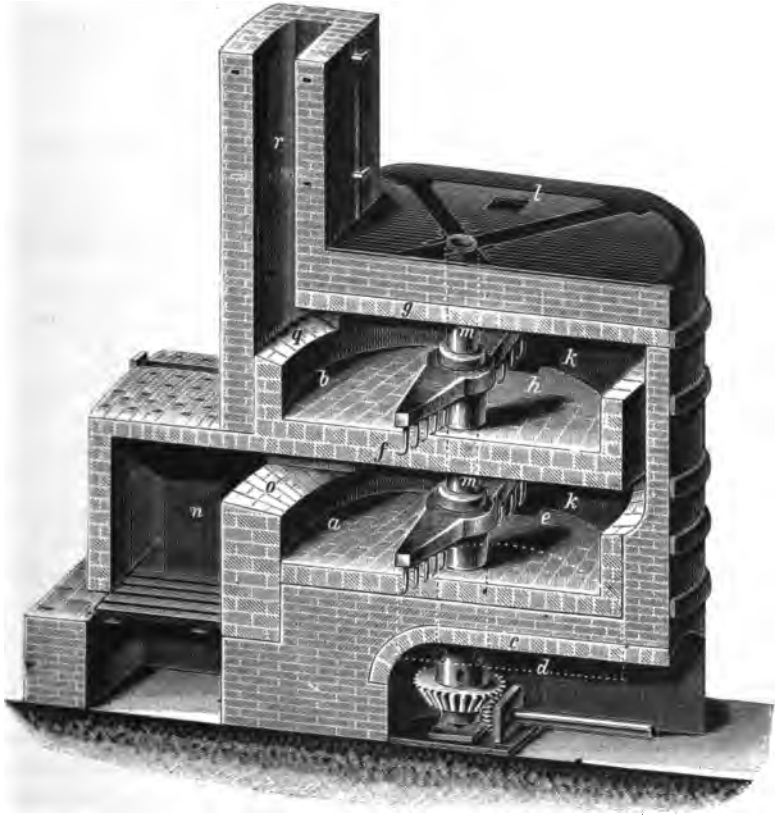


Fig. 59.

pass through a flue from the lower to the upper hearth, thence by the flue *q* to the stack *r*. Instead of the two hearths a single hearth has been used, with hollow rabbles through which air is forced by means of a fan. At Eitorf, in such a furnace, 10 feet in diameter, 4 to 5 tons of ore were roasted in twenty-four hours.

The capacity of these furnaces is inferior to that of the O'Harra furnace and of those with revolving cylinders; they are accordingly

only used when an extremely careful calcination is required, *e.g.*, for the Ziervogel process at Mansfeld.

CALCINATION IN REVERBERATORY FURNACES WITH MOVABLE BED

Calcining furnaces with movable beds or hearths, and fixed or movable rabbles, are but rarely used for calcining copper ores on account of their relatively small capacities. Brunton's calciner[1] is used for the roasting of tin ores containing arsenical pyrites, that of Gibbs and Gelstharp[2] for the chloridising roasting of cupriferous pyrites residues.

CALCINATION IN REVERBERATORY FURNACES WITH MOVABLE WORKING CHAMBERS

Calciners of this class are rotating cylinders that work either intermittently or continuously. They roast thoroughly with a moderate consumption of fuel and very low labour costs. They are used to advantage in countries like the United States and Australia, where wages are high ; they are also used in England.

The Brückner furnace is the typical intermittent revolving furnace ; 180 of these are employed at the Anaconda Works, Montana, where the author saw them in operation. The construction of the furnace is shown in Figs. 60 and 61. *A* is a revolving wrought-iron cylinder, lined with firebrick, which is set in motion by means of the wheels *G* and *H*. *B* is the fireplace, *D* the flue, and *C* a flue that also serves as dust-chamber. *F F* are hoppers, from which the charge is dropped into the cylinder through the doors *E E*. When the calcination is finished, the ore is discharged through these doors into waggons *J J*.

The Brückner cylinders at Anaconda, as built by Messrs. Fraser and Chalmers, are 18 feet 6 inches long and 8 feet in diameter inside. The cylinders are turned merely by the friction of the carrying wheels against rings on the cylinders, the power required being 2 horse-power. In sixteen hours each furnace will roast 12 tons (equal to 18 tons in twenty-four hours) of copper ores, with 38 per cent. of sulphur down to 9 per cent., with a consumption of $1\frac{3}{4}$ cords of wood. Six workmen can attend to nine furnaces on each shift. At Anaconda groups of sixty furnaces are built under one roof. For the calcination of 9 tons of ore 1 ton of coal would suffice. These figures show the superiority of the Brückner furnace over the hand-worked calciner, where fuel and labour are both dear.

[1] *Allgemeine Hüttenkunde*, p. 432.
[2] *Ibid.* p. 433.

Continuously working furnaces consist of an inclined cylinder of cast or wrought iron, provided with an automatic charging arrangement. Ore is continually charged at the higher—the fluebridge—end of the furnace, and passes gradually through the slowly revolving cylinder till it drops roasted from the lower end. By means of longitudinal projections of firebrick in the interior of the lining the

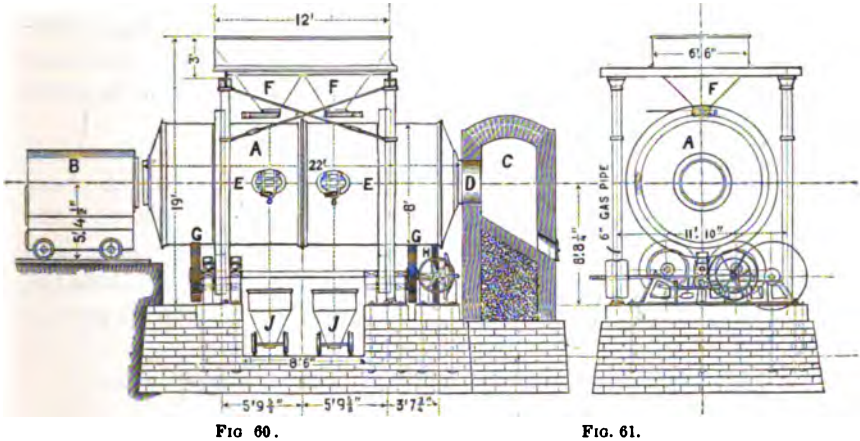


FIG 60.

FIG. 61.

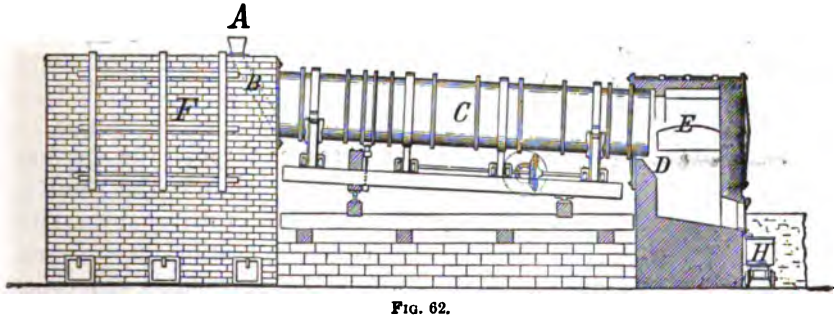


FIG. 62.

distribution of the ore, and thereby its calcination, is facilitated. Such furnaces have been designed by White, Howell, Hocking, and Oxland, and have been chiefly employed in the chloridising roasting of silver ores. They are, however, well suited for calcining copper ores, and are characterised by thorough calcination, low consumption of fuel, and especially low cost of labour.

The White calciner is shown in Fig. 62; *C* is the cylinder, *A* the ore feeding arrangement that continuously delivers ore into *C*, whence it finally drops out at *D* into the waggon *H*. The fire-place is in the

chamber *E*; the gases pass out at the upper end of the cylinder into the dust-chamber *F* and thence to the stack. Longitudinal ribs projecting from the lining raise the powdered ore and allow it to fall through the heated gases as soon as its angle of repose is exceeded; the necessary amount of air enters either through the firing door or through special openings. Different degrees of inclination, to suit different ores, can be given to the cylinder.

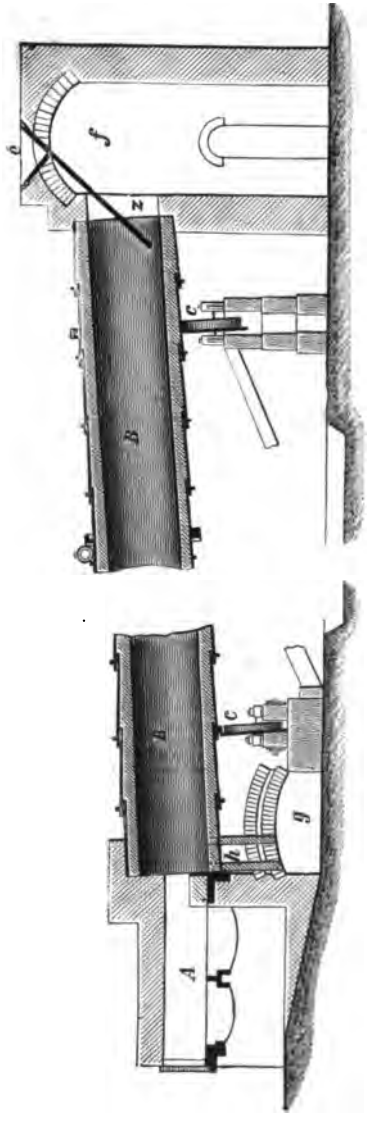


FIG. 63.

The Hocking-Oxland furnace is represented in Fig. 63. *B* is the cylinder, *A* the fire-place, *z* the flue, *f* the dust-chamber. The ore is automatically fed into the cylinder through the hopper *e*,

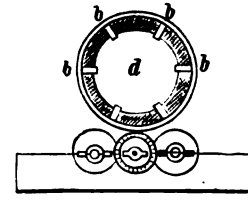


FIG. 64.

and escapes through the slot *h* at the lower end, into the vault *g*. The cylinder is driven by a tangent screw gearing in a worm wheel that surrounds the cylinder; *c c* are friction wheels. This cylinder, like the last, can be raised or lowered as required. Fig. 64 shows a cross section of the furnace showing the firebrick lining *a* and the six projecting firebrick ribs, *b b b*.

The author has seen these furnaces used for roasting copper ores at the copper works at Wallaroo, South Australia. The furnaces are 40 feet long and 4 feet in diameter inside, without lining; they have eight rows

of firebrick ribs. They are driven by worm gearing and are carried on three sets of friction rollers. In twenty-four hours a furnace will roast twelve tons of pyritic copper ores from 25 per cent. down to 4 per cent. of sulphur, the coal consumption being 5 per cent. of the weight of the raw ore, an equal amount being required to generate the necessary power. One man attends to a pair of furnaces on each shift.

As is shown by the above figures, continuous acting rotating calciners effect marked economies over the handworked calciner with fixed bed when wages and fuel are high.

CALCINATION IN MUFFLE FURNACES

Muffle furnaces (*Gefässöfen*) are employed when it is desired to manufacture sulphuric acid (or when sulphur fumes may not be allowed to escape freely) from ores which cannot be roasted in shaft furnaces because of their fritting, melting or decrepitating. They have the disadvantage as compared with shaft furnaces, that they use considerably more fuel and that the ore must be in a state of fine powder. Compared with reverberatory furnaces they labour under the disadvantage of smaller capacity and of greater consumption of fuel and heavier outlay for labour. Nevertheless they may be used to great advantage for ores of the above character, when these ores require effectual calcining whilst their gaseous products are to be used in the manufacture of sulphuric acid.

Muffle furnaces may be divided into those with fixed and those with rotating working-chambers. Of the former class the Hasenclever furnace, which is used successfully at Oker for the calcination of copper ores, is the best known.

The Hasenclever furnace consists of several muffles lying one above the other and connected by vertical flues, which are heated by means of a fire-place. The ores to be roasted are charged through a hopper into the uppermost muffle, in which it is pushed along from time to time like the charge in a fixed-bed calciner; when it reaches the end of this muffle it is dropped through a vertical flue into a second one, along which it also passes, to be dropped into a third muffle, from which it is ultimately withdrawn through a working door. The flame travels the opposite way to the ore, from below upwards, passing along the floors and roofs of each muffle in turn. More recently two muffles have been laid directly one on the other the flame passing under the floor of the lower and over the roof of the upper one. A pair of Hasenclever furnaces are shown in Figs. 65

and 66. *R* is the grate of one of these furnaces; *MM* are the muffles; *FF* are the flues for the flame which passes in the direction shown by the arrows; *AA* are the charging doors for the ore; *w* are the working doors. The gases evolved during calcination pass hrough the apertures *a* into the vertical flue *b*, thence to the main

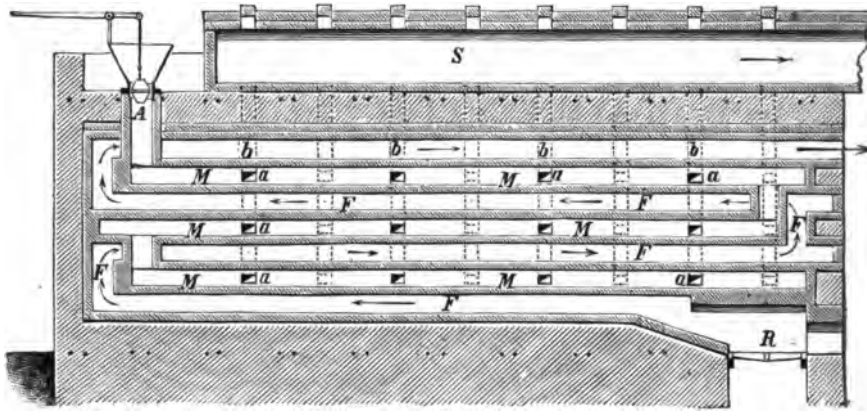


FIG. 65.

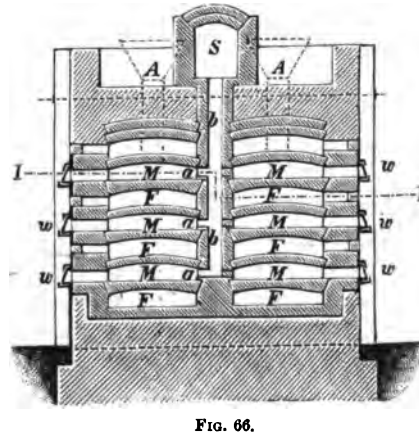


FIG. 66.

flue *S* which leads to the sulphuric acid chambers. Each furnace is 33 to 36 feet long and 10 to 13 feet high and wide. The Rhenania Company of Stolberg, near Aachen (general manager, Hasenclever), undertakes the erection of these furnaces and will furnish all details.

At the Oker Works a Hasenclever furnace with 3 muffles will roast in 24 hours 3½ tons of lead-bearing pyritic copper ores, or 4

tons of pyritic ores rich in copper down to 3 per cent. of sulphur with a coal consumption equal to 30 per cent. of the weight of the ore for the former and 27 per cent. for the latter class of ores. Each furnace requires 2 men on each shift.

Copper ores have hitherto not been calcined in the muffle furnaces of Liebig and Eichhorn, nor in that of Grillo, although they would answer as well for this purpose as for that of roasting zinc blende, for which they have up to the present been used.

The other muffle furnaces with fixed muffles consume such a large amount of fuel that they are not likely to be applied to the roasting of copper ores.

Revolving muffle furnaces have not so far found any definite application for calcining copper ores. The furnace proposed for this purpose is the *Douglas furnace;* it consists of an inclined rotating cylinder, in the axis of which runs a chamber of cast iron or firebrick. The products of combustion traverse this chamber whilst the powdered ore is charged into the space between it and the lining of the cylinder. As the ores are heated by radiation, they are roasted without coming into contact with the products of combustion, and the sulphurous gases evolved can accordingly be used to manufacture sulphuric acid. In order to keep the ore in movement, the space between the cylinder and the central chamber is divided into four by means of four longitudinal partitions made of firebrick, traversed by openings. These partitions raise the ore which can fall through the openings from one compartment to the other. The ores are charged automatically at the upper end and are delivered at the lower end of the cylinder.

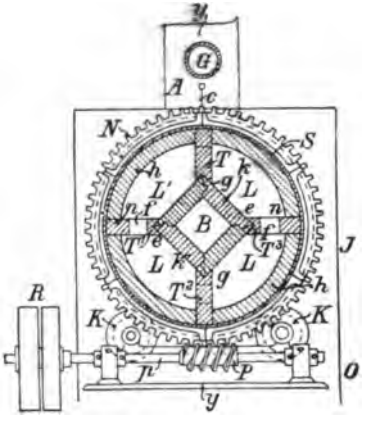


FIG. 67.

The construction is shown in Figs. 67 and 68. *S* is the inclined rotating cylinder driven by worm gearing. In it runs the chamber *B* opening into the fire-place *D*. It is connected to the cylinder by means of the partitions *T*, T^1, T^2, T^3, and rotates with it. The walls of the chamber, the partitions and the lining of the cylinder are composed of firebrick. *A* is the stack with which the chamber *B* communicates. The ores are charged by the hopper H^2, and fall from

the lower end of the cylinder into the chamber *E*. *C* is a branch flue that connects the fire-place with the stack when it is required to cool down the chamber *B*; to effect this the damper *c* is closed and *d* and *a* opened. Cold air then enters through the flue *C*, traverses the chamber *B*, and passes from it through *G* to the stack *A*. By closing the damper *b* the heated gases from the fireplace are cut off. By means of an adjustable damper, not shown on the drawing, the admission of air to the ore is regulated.

Few data are yet available as to the results obtained by this

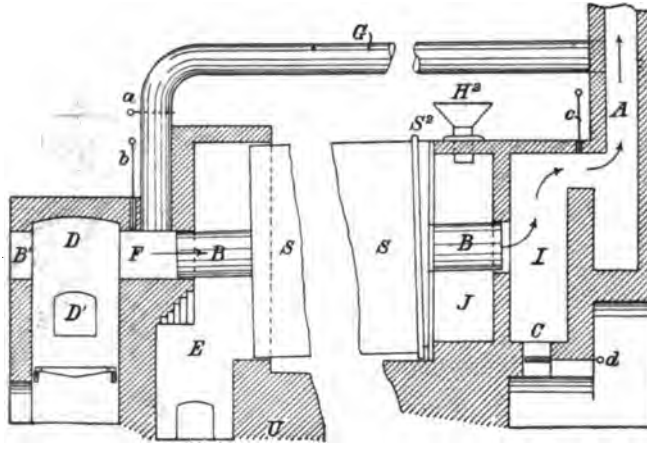


FIG. 68.

furnace. It has been used to calcine pyritic fines, and its maximum capacity seems to be 12 tons of such ore roasted in 24 hours down to 3 per cent. of sulphur.

SMELTING THE CALCINED ORE FOR MATTE IN SHAFT FURNACES

Calcined copper ores consist of a mixture of oxides, sulphates and undecomposed sulphides of copper and iron, in which the greater part of the copper is combined with sulphur. Other frequent constituents are sulphates, oxides and undecomposed sulphides of zinc and lead, arsenides and antimonides, arseniates and antimoniates, together with quartz, silicates, and sulphates of lime and baryta.

By smelting these ores with carbon and suitable fluxes, the iron is to be slagged off as far as possible and all the copper collected into a matte or regulus. The iron is slagged by the reduction of the

peroxide to protoxide and the combination of the latter with silica, together with the decomposition of sulphide of iron by oxides of copper in the presence of carbon and silica. Oxides and silicates of copper are thus transformed into sulphide whilst a corresponding quantity of iron appears as silicate, as shown in these equations:

$$2CuO + 2FeS + SiO_2 + C = Cu_2S + FeS + FeSiO_3 + CO$$
$$4CuO + 3FeS + SiO_2 + 2C = 2Cu_2S + FeS + Fe_2SiO_4 + 2CO.$$

A portion of the oxides of copper is reduced to metal by carbon and carbon monoxide, the copper reducing some of the sulphide of iron, either to metallic iron or possibly to a subsulphide:

$$2Cu + FeS = Cu_2S + Fe \text{ or } 2Cu + 2FeS = Cu_2S + Fe_2S.$$

As the existence of subsulphide of iron (Fe_2S) has not yet been proved it is better to assume that the former reaction alone takes place, the metallic iron being dissolved by the matte, the possibility of which has been proved with certainty. It is also possible that some of this metallic iron reduces ferric to ferrous oxide, which is then slagged off, thus: $Fe_2O_3 + Fe = 3FeO$. Sulphate of copper is reduced to sulphide. Besides the above main reactions, those of the English process, namely, the interaction of oxide of copper with sulphides of copper and iron, occur to some extent as secondary reactions.

The whole of the sulphide of copper present unites with the sulphide of iron that remains undecomposed to form matte. As long as sufficient sulphide of iron is present, no copper can pass into the slag as silicate, because the latter would be decomposed by sulphide of iron forming sulphide of copper and silicate of iron.

Oxide of zinc is partly reduced to metallic zinc and volatilised, and partly passes into the slag. Sulphide of zinc goes partly into the matte, but principally into the slag. Sulphate of zinc is partly split up, leaving zinc oxide, partly reduced to sulphide. (Zinc oxide and sulphide interact like the corresponding copper compounds.) Lead is reduced from its oxide and sulphate to metal or to sulphide and passes into the matte. Any silver present in the ore likewise goes into the matte.

Antimoniates and arseniates are reduced in part to antimonides and arsenides, in part to the metallic state and volatilised; in the presence of iron pyrites some of the arsenic is volatilised from arsenides as sulphide of arsenic. The remaining antimonides and arsenides pass into the matte when they are present in small quantities only; otherwise they separate from it, forming speiss

(*speise*). Barytes and gypsum are reduced to sulphides and react like sulphide of iron with the oxidised copper compounds. Sulphide of barium may also pass into the matte.

Barytes, sulphide of iron and silica interact at high temperatures, the silica displacing the sulphur trioxide of the first named, which, splitting into sulphur dioxide and oxygen, oxidises the sulphide of iron forming ferrous oxide and sulphur dioxide. The double silicate of baryta and iron thus formed is readily fusible; this same silicate is formed by the action of silica and metallic iron upon barytes.

Quartz and silicates, which constitute a part of the ores, are slagged off. In order to produce suitable slags, when the ore is acid, that is to say, contains siliceous and clayey matter, the fluxes to be added must be basic, and consist generally of ores rich in iron and lime, as also of basic slags produced in working mattes and coarse copper. When the ores are basic, as in the case of ores rich in oxide of iron, the fluxes used are siliceous and clayey ores, acid slags, clay and clay slate. Ores that have been too completely roasted, and which would therefore produce coarse copper, are mixed with raw ores, whilst ores that have not been roasted very much and which would therefore give a large quantity of poor matte, are mixed with oxidised or acid ores and copper refinery slags.

The sulphur contents of the charge are so calculated as to yield a matte with between 35 per cent. and 50 per cent. of copper. When the copper falls below 35 per cent., the quantity of matte produced is too great and the cost of its further treatment comes too high; when it rises above 50 per cent., the slag is found to be too rich in copper, and cannot be thrown away.

The slag produced during smelting must separate readily from the matte so that it may not retain any particles (*prill*) of the latter mechanically intermixed, nor may it contain any copper chemically combined. Normal slags may be said to be such as are intermediate between mono- and bi-silicates, and contain ferrous oxide as the principal base. When the ores carry much iron and zinc, the slags are made more basic (mixtures of sub- and mono-silicates, or pure mono-silicates), whilst, when they contain much silica, the slags are made more acid (bi-silicates or mixtures of bi- and tri-silicates). Thus slags of the former type are produced with pyritic copper ores, which consist chiefly, after calcination, of oxide of iron. If more silica were added than the above proportion indicates, the amount of slag produced, and with it the cost of smelting and the loss of copper in the slag would be increased. Such slags are also produced when zinc is present in the ores, because basic ferriferous slags have the property

of dissolving considerable quantities of oxide and sulphide of zinc without at all impairing their qualities. (Any oxide of zinc that is not slagged off is reduced and volatilised, and being again oxidised, is deposited on the walls of the furnace, forming the so-called *furnace calamine*, the presence of which greatly reduces the length of the smelting campaign.) Larger quantities of sulphide of zinc form with the slag and a portion of the matte, a porous mass called *skumnas* (scum or foam) in Sweden, from which the copper can only be extracted with great difficulty. It is therefore advisable to convert the sulphide of zinc as far as possible into oxide during the roasting and to decompose any basic sulphate of zinc that may form, by mixing carbonaceous matter with the ore during calcination.

Bi-silicates are produced when the ores are rich in silica, to save the expense of handling large quantities of slag and also the cost of fluxes, seeing that very considerable quantities of bases are needed to produce slags low in silica (60 parts of SiO_2 require 72 parts of FeO to form a bi-silicate, but 144 parts to form a mono-silicate).

Mixtures of bi- and tri-silicates are only exceptionally produced, as in smelting the Mansfeld *Kupferschiefer*, which contains the substances in the proportions requisite to form such a slag, and which, with its very low copper contents (2 to 3 per cent.), could not support the extra expense of adding barren fluxes.

Too high a proportion of silica has its disadvantage quite as much as too low a proportion or too high a proportion of iron.

The former condition makes the slag difficultly fusible, so that it is apt to mechanically enclose particles of matte, especially when it is very pasty. The great objection is, however, that at the high temperature needed to fuse the slag, a certain amount of iron is reduced, just as it is from ores or even from silicates in the blast furnace. This iron may be deposited either in the upper parts of the shaft or on the hearth bottom as a *bear*, and in either case may bring about the chilling of the furnace. Furthermore, when the charge is too rich in silica, the consumption of fuel is increased and the capacity of the furnace diminished. Quartzose ores, poor in copper, should either be reserved for the English process of smelting, or, when this cannot be done, they are best treated by wet methods. Unless in exceptional cases, as in the above cited instance of Mansfeld, experience has shown that the silica in the slags should not exceed 42 per cent.; even when it exceeds 36 per cent. the working capacity of the furnace is found to decrease, without, however, any other injurious effects being perceptible, up to the 42 per cent. limit.

Too low a percentage of silica, or too high a percentage of iron

increases the specific gravity of the slag, so that it does not separate readily from the matte and is apt to enclose particles of the latter. Such slags also attack the brickwork of the furnace, dissolving its silica and acid silicates. Moreover metallic iron is easily reduced from slags rich in that metal, and this iron forms bears on the hearth bottom and thus shortens the smelting campaign. Although low silica is not as injurious as high silica in a slag, experience has shown that it is best kept above 24 per cent., whilst 18 per cent. is looked upon as the minimum amount admissible.

The best results are obtained when the percentage of silica is between 24 and 36.

As bases, there may be present, in addition to ferrous oxide, lime, magnesia and alumina. Even comparatively small amounts of the two latter render the slag difficultly fusible, whilst considerable proportions of the former do no harm.

The composition of a number of slags with varying proportions of silica is shown in the subjoined table :—

Locality.	Oker.	Oker.	Röros.	Altenau.	Fahlun.	Mansfeld.	Mansfeld.	Mansfeld.
Character of slag.	Sub-silicate.	Mixture of sub- and mono-silicate.	Mono-silicate.	Between mono- and bi-silicate.	Between mono- and bi-silicate.	Bi-silicate.	Between bi- and tri-silicate.	Between bi- and tri-silicate.
Silica	21·62	25·24	31·44	34·67	40·28	48	54·18	57·43
Alumina . . .	5·15	14·00	7·86	4·38	12·20	15	10·53	7·83
Lime	2·57	4·86	—	3·53	—	20	19·41	23·40
Magnesia . . .	—	—	4·46	—	2·67	5	1·79	0·87
Ferrous oxide .	65·62	45·96	55·21	48·25	49·80	5	10·83	7·47
Oxide of zinc .	—	6·40	—	2·89	—	—	—	—
Cuprous oxide .	2·26	0·3 to 0·5 Cu.	—	—	—	—	2·03	0·30
Manganous oxide	—	—	—	2·00	—	—	—	—
Oxide of lead .	—	—	—	1·07	—	—	—	—
Sulphur . . .	2·08	—	—	—	—	—	—	—

The shaft furnaces, in which the roasted ores are smelted, have undergone numerous modifications within the last forty years, low furnaces with vertical distribution of the charge having been exchanged for higher furnaces with horizontal distribution. The square or trapezoidal cross-section has been replaced by circular, rectangular or elliptical sections. Instead of the furnace tapering upwards from the tuyeres to the throat, it is slightly widened or kept uniform in section throughout. Instead of furnaces held together with massive retaining walls, difficult of access, furnaces now stand free on light supports with slight outer walls, or the latter are replaced by iron shells, or again the brickwork is replaced by hollow iron boxes through which water circulates (water-jacket furnaces). The working capacity of the furnaces has been increased by employing larger dimensions, a

greater number of tuyeres, higher blast pressures, and by injecting greater volumes of air.

As regards the height of the furnace, this depends chiefly on the amount of iron in the charge and the nature of the fuel. The higher the furnace the more readily is iron reduced from the charge, wherefore lower furnaces are used for ores rich in iron than for ores poorer in that metal. Other things being equal, a furnace using charcoal should be higher than one using coke, because charcoal has a great tendency to burn upwards, and with a low furnace a portion of the fuel would burn to waste uselessly in the throat. With ores containing much zinc, if all this metal cannot be slagged off, some may have to be volatilised, in which case the furnace is not made too high for fear of accretions forming in the upper part of the shaft. Generally speaking, the height of modern furnaces varies between 11 feet 6 inches and 30 feet from the floor level to the throat. The latter height is quite exceptional, and is only used for ores rich in silica and earths, poor in iron and difficultly fusible, where there is little fear of iron being reduced, as for instance at Mansfeld. The distance between the level of the tuyeres and the throat, which controls the height of the furnace, is there about 21 feet 6 inches. For basic ores rich in iron (calcined pyrites) this distance varies between 8 feet and 13 feet; thus for smelting cupriferous pyrites with 3 per cent. to 4 per cent. of copper, in the United States it is 10 feet. For more acid ores this figure varies between 13 feet and 16 feet 6 inches, according to the proportion of silica present. In the United States, when acid ores are to be smelted, it is found preferable not to exceed 14 feet, because otherwise metallic iron might be reduced.

According to Bredberg, when charcoal is the fuel employed, the furnace should be at least 20 feet 6 inches high; such furnaces were formerly in use at Atvidaberg in Sweden. The cross-section of modern furnaces is circular, rectangular or oval.

Circular furnaces cannot exceed a given diameter, otherwise the blast, at any admissible pressure, would not penetrate to the centre of the furnace. The pressure on the other hand depends on the fusibility of the ores and the amount of iron they contain. At high pressures iron is apt to be reduced, and the more readily, the richer the charge is in iron. With ores poor in iron the pressure may be moderately high and the diameter of the furnace be correspondingly increased. The diameter at the tuyere level, which principally influences the output of the furnace, must not, however, be too great when difficultly fusible ores, such as ores poor in iron, are being treated, for fear of imperfect fusion; the diameter at the tuyere level

is accordingly considerably reduced when this class of ores is to be smelted. Of all modern circular furnaces those at Mansfeld, designed for treating the difficultly fusible ores of the district, have the largest diameter and are worked at a blast pressure of 2·9 to 4·3 inches of mercury. The diameter of these furnaces at the tuyere level is from 5 feet 3 inches to 6 feet 2 inches, and 7 feet 3 inches at the throat. The quantity of ore treated varies from 100 tons at the lower blast pressure to 150 tons at the higher, in twenty-four hours. For easily fusible ores the blast pressure ranges from 0·8 to 1·6 inches of mercury, according to the character of the ores; the diameter at the tuyere level should then be between 2 feet 6 inches and 4 feet 6 inches, increasing a little towards the throat. For example, the circular furnaces at Oker, in the Lower Harz, are 4 feet 3 inches in diameter at the tuyeres and 5 feet 9 inches at the throat, working at a blast pressure of 1·4 inches of mercury; at Brixlegg, in the Tyrol, the diameter is 4 feet at the tuyeres and 5 feet 6 inches at the throat, and the American water-jacket furnace with a blast pressure of ½ to ¾ lb. on the square inch has a diameter at the tuyeres varying from 3 feet 6 inches to 4 feet 2 inches.

Rectangular and oval furnaces are better suited for large outputs than circular furnaces, because, although the shorter side or diameter is fixed by the nature of the ore, the area at the tuyere level, upon which the output of the furnace depends, can be increased by lengthening the longer side or diameter as much as possible. Such furnaces have found much favour in the United States, and have, with the exception of the Mansfeld furnaces, the largest capacities (90 tons in twenty-four hours) of any shaft furnaces hitherto constructed for smelting calcined ferriferous copper ores. The greatest length of the rectangle is 11 feet 6 inches in the clear, in the Orford furnaces, whilst the width should not greatly exceed 3 feet 3 inches, being 3 feet 6 inches in the furnaces in question.

The walls of the furnace are either perpendicular as in the Orford furnace, or else widen out towards the top, when the furnace becomes a Raschette furnace. Rectangular furnaces are also built with water-jackets, the form known as the Henrich furnace being in use in the United States. Water-jackets are constructed either of cast or wrought iron, the latter having given the better results in the United States.

An improvement on the rectangular furnace has been the rounding off of the corners, when the section approaches that of an ellipse. This improvement was introduced in Russia by Skinder for brick furnaces, and for water-jackets by Herreshof at Brooklyn, where the

author has seen them in operation. The Herreshof furnace widens upwards; it is 6 feet 4 inches long by 3 feet 6 inches wide at the bottom, 7 feet 4 inches by 4 feet 7 inches at the throat, and 6 feet 6 inches by 3 feet 8 inches at the tuyere level. Its plan is that of a rectangle, with sharply-rounded corners, and the longer sides curved outwards. This furnace has a capacity of about 90 tons of roasted cupriferous pyrites in twenty-four hours, and the water-jacket of this shape is found to wear longer than it does when rectangular.

In the modern furnace, the tuyeres are distributed as symmetrically as possible round the periphery of the furnace; in the older system of charging in vertical columns and smelting with a *slagnose* (a prolongation of slag on the end of the tuyere) the tuyeres, from one to three in number, were placed in the rear wall of the furnace. Modern furnaces have not less than three, and up to as many as fourteen tuyeres; thus the Oker furnaces have five, the Mansfeld furnaces six, the Herreshof furnaces thirteen, and the Orford furnaces fourteen tuyeres. As a rule the tuyeres are cooled by water, the Skinder and Orford furnaces being the only exceptions.

As already stated, the blast pressure varies when coke is used between 0·8 and 1·6 inches of mercury (about 0·4 to 0·8 lb. on the square inch) and is only exceptionally (at Mansfeld) as high as 3·9 inches of mercury. The pressure must be less when charcoal is used as fuel.

The blast is generally produced by means of blowers, Root's blower being used in Europe and Baker's blower in America and Australia. Blowing engines and the *Cagniardelle* (a blowing machine consisting of a rotating air-chamber dripping diagonally into a water-tank) are only used exceptionally for very high furnaces and difficultly fusible ores, as at Mansfeld. Hotblast, too, can only be employed with advantage under the same exceptional circumstances, because it would otherwise tend to reduce iron from the ore. At Mansfeld the blast is heated up to between 200° and 300°C. by means of the furnace gases.

There are three types of furnaces in use :—

Spurōfen, or furnaces with independent forehearths.

Tiegelōfen, or furnaces with crucibles and no forehearths.

Sumpfōfen, or furnaces with fixed forehearths of the syphon pattern continuous with the crucibles.

Furnaces with independent forehearths are used with advantage in smelting highly ferriferous ores, such as roasted pyrites, where there is danger of iron being reduced and forming sows on the furnace bottom, should the molten materials remain too long in the furnace.

The objection of an imperfect separation of slag from matte in independent receivers outside the furnace proper may be got over by running the molten matter direct into covered receivers, in which the temperature is sufficiently high to keep the contents fluid so that the matte can separate sharply from the slag. The slag is allowed to flow off continuously through a slagnotch provided with a spout, whilst the matte is either tapped out periodically, or is allowed to run continuously at a lower level than the slag. A continuous flow of matte is obtained by dividing the receiver or forehearth into two compartments by means of a firebrick wall, at the bottom of which a slot forms the means of communication between the two divisions. This slot is kept closed until the compartment that communicates with the interior of the furnace is filled with matte, so that no slag can pass through the slot, which is then opened, when the matte rises to the same level in each compartment. The matte is then allowed to run continuously, through a hole provided with a spout, from the second compartment, whilst the slag flows at a higher level from the first compartment. These arrangements further possess the advantage that they prevent the blast blowing through the tap hole, whilst the furnace bottom is kept free from bears and accretions, which are deposited in the forehearth. This system is used to great advantage in the United States; much skill is, however, required in the management of the furnace, and the outlet can only be kept from chilling by putting through very large quantities. The first-named arrangement is combined with the Herreshof, the second with the Orford furnace; each will be described in detail under the head of the respective furnaces.

On the continent of Europe forehearths either take the form of the so-called *brillenofen* (= "spectacle" furnace), so called because it has two outlets—called the "eyes" of the furnace in German—side by side, or else they are furnaces provided with simple outside pots, both forms being lined with a charcoal brasque. In small furnaces the matte is allowed to set partially in the pot or forehearth, and then a disc of chilled matte is lifted off the surface; in larger furnaces, the pot is allowed to fill with matte, and is then tapped. In either case the separation of matte from slag is less perfect than in the American method; the matte pots are, however, more readily cleaned out and repaired than are the American forehearths.

Furnaces with closed crucibles and without forehearths should be used when there is no fear of iron being reduced from the ores and forming bears and accretions; they keep the heat well together and maintain the contents of the furnace in a state of thorough

fusion, which allows the matte to separate sharply from the slag. The slag is either allowed to flow continuously into slag pots, or is tapped at a suitable level at definite intervals of about ten minutes alternately through two slag notches. In the latter method, which is the rule in the Western States of North America, the heat is thoroughly retained in the furnace, and the slag remains very liquid, and separates most perfectly from the matte; it is moreover so hot that it can run through several vessels placed one below the other, at the bottom of which any matte, that might have been carried over, will settle.

At the Mansfeld works, the slag traverses two iron boxes, set one below the other, and runs thence into movable slag pots. Any matte settles in the two boxes, whence it is tapped off from time to time. The objections to the crucible hearth are the formation of hollow spaces, and the escape of blast through the tap hole, when the matte is tapped off.

Furnaces that are continued into forehearths, which are not removable, but form a part of the furnace proper, are employed with charges rich in both iron and zinc, that necessitate a frequent clearing out of the lower part of the furnace to remove accretions. The matte does not separate so freely from the slag as in the last-named type of furnace, and the slag is not hot enough to traverse several receivers and deposit therein any matte it may be carrying, so that this type of furnace should only be used when the formation of accretions makes it absolutely necessary. At the same time it must be remembered that substances can be thoroughly fused in the greater heat of the crucible furnace which would form accretions in this type. With very high contents of iron together with zinc in the ores, crucible furnaces cannot be used because of the reduction of iron in them. For such ores movable fore-hearths should be employed when possible, but if not then these fixed fore-hearths must be used. They have the same disadvantages too, as crucible furnaces, in permitting the formation of hollows and the escape of blast.

The matte, that flows, or is tapped from shaft furnaces, is run into sand moulds, brasqued pots or iron moulds.

The fuel is either coke or charcoal, the former carrying heavier burdens and standing higher blast pressures than the latter. A ton of ore requires according to its nature from 2 to 8 cwt. of coke.

Typical examples of various furnaces constructed according to the above principles will now be given.

Older Furnaces

The older furnaces have been almost completely displaced by the more modern types, with numerous tuyeres, charged in horizontal layers, and possess, therefore, scarcely more than a historic importance; they will accordingly be only briefly mentioned. The *Krummofen* is a low furnace, capable of being charged from the floor level of the works, square or trapezoidal in cross section, with two tuyeres in the back wall; the mode of charging is vertical. These furnaces consume much fuel, since they work with hot throat (*i.e.*, the furnace gases burn at the throat), require much labour and lose much metal. The author has still met with them in operation in

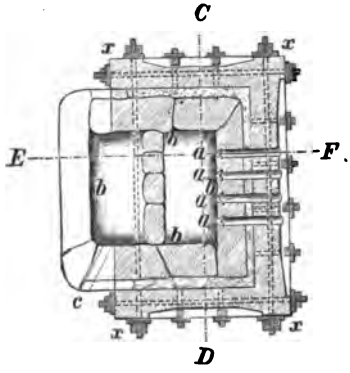


Fig. 69.

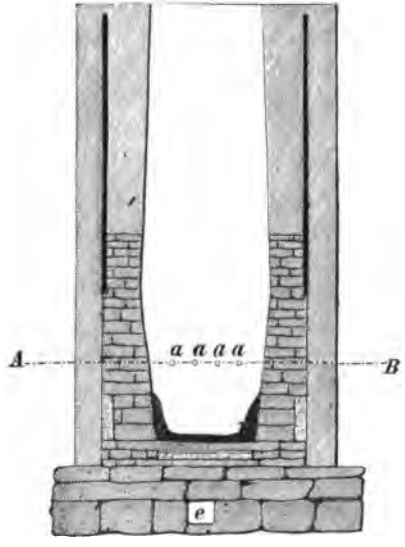


Fig. 70.

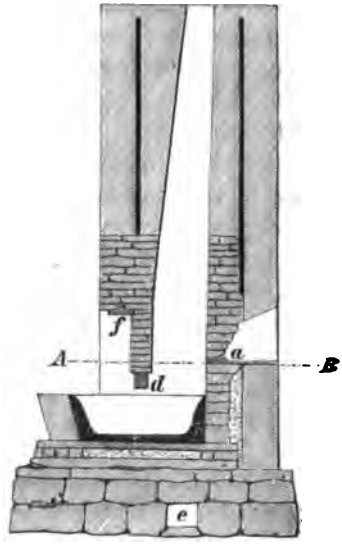
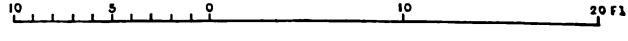


Fig. 71.



various works in Transcaucasia (Allawerdi near Tiflis and Kaward and Katar in Karabach). They have a fixed fore-hearth. The blast was pro-

duced by means of leather bellows, worked by hand whenever water power was not available.

The *Sulu furnace* ("Sulu" is the Swedish term for ore that has been fritted together by calcination) was formerly employed at Atvidaberg, Fahlun and Sala in Sweden. A furnace of this kind, as formerly employed in Atvidaberg, is shown in Figs. 69 to 71 after Bredberg. It had a fixed fore-hearth *b* lined with charcoal brasque, was rectangular in plan and had four tuyeres, *a*, in the rear wall; *d* is an iron bearer upon which the breast of the furnace was supported; *c* is the tap hole. It was 23 feet 3 inches high, and used charcoal as fuel. To promote uniform descent of the charge the shaft was divided by a vertical partition. This furnace was

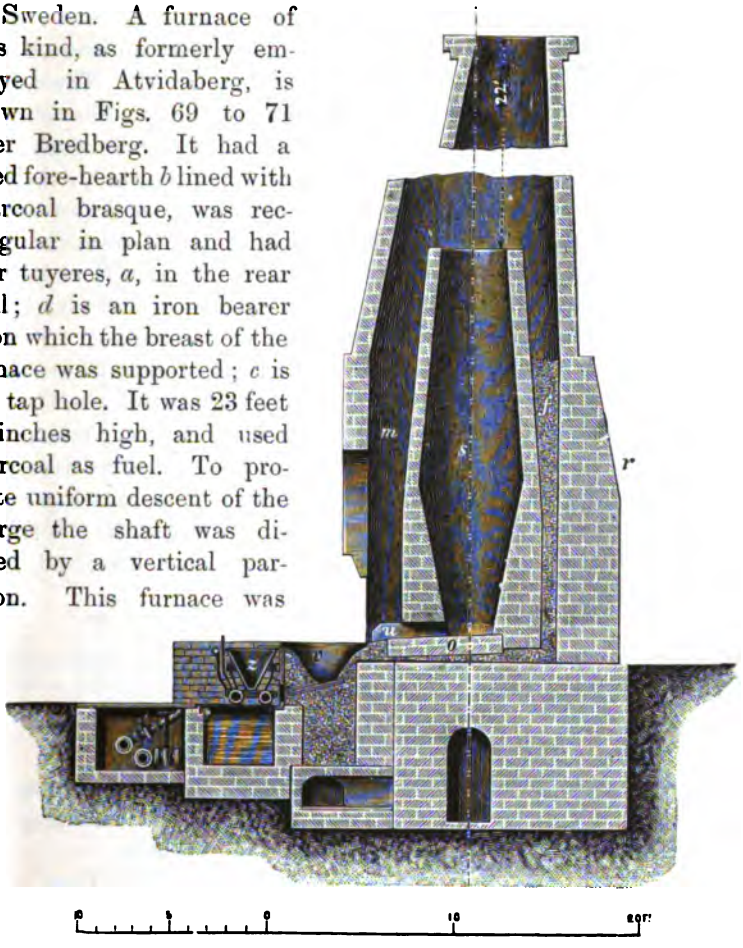


FIG. 72.

subsequently replaced by one with five tuyeres, three in the rear wall and one in each side wall.

The old furnaces of the Lower Harz had one or two tuyeres in the rear wall, a fixed fore-hearth, and were trapezoidal in plan. The front wall was vertical, whilst the back wall sloped towards it going upwards, so that the furnace tapered upwards.

The older Mansfeld furnaces for smelting the *Kupferschiefer* were

divided into the so-called *low furnaces* and *high furnaces.* The former had a fixed fore-hearth and two tap holes, their height varying from 14 feet 5 inches to 16 feet 6 inches; the shaft was trapezoidal in plan, narrowing somewhat downwards. Blast was supplied through one tuyere in the rear wall. The charging was in vertical columns.

The high furnaces were from 18 feet 6 inches to 20 feet 7 inches high, had independent fore-hearths and boshes like an iron smelting blast furnace. Their construction is shown in Fig. 72. The number of tuyeres was at first two, and subsequently three. The charging was by horizontal layers. In the figure, *s* is the inner shaft, *f* the so-called *filling* between the shaft walls and the outer walls, *r* the outer wall, *o* the hearth stone, *u* the tap hole block, which separates the two eyes or tap holes, *m* a chimney for drawing off fumes from the working side of the furnace, *v* one of the pair of receivers (fore-hearths) for the collection of the molten materials. The slag flows from these receivers into slag pots *z*, whilst the matte was tapped off into a a granulator; the latter was used for some time in Mansfeld to enable the matte to be more readly pulverised for the Gerstenhöfer Calciner. These furnaces have been replaced by the modern circular furnaces.

The older Russian furnaces (Siberian furnaces) such as were being used at Kedabeg in the Caucasus whilst the author was there, were rectangular in plan and had six tuyeres in the rear-wall; the furnace was about 16 feet 6 inches high, 7 feet 6 inches long, and 2 feet 3 inches wide.

Modern Furnaces

These are round, rectangular or oval in plan, with symmetrically distributed tuyeres, and are charged in horizontal layers.

FURNACES OF CIRCULAR CROSS-SECTION

These have been built after the pattern of the Pilz furnaces used for smelting lead ores.

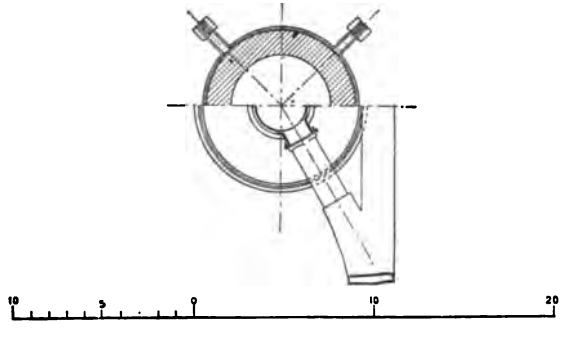
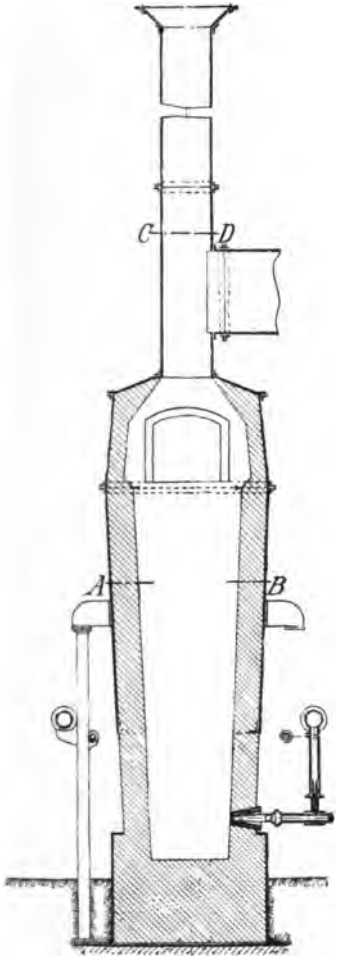
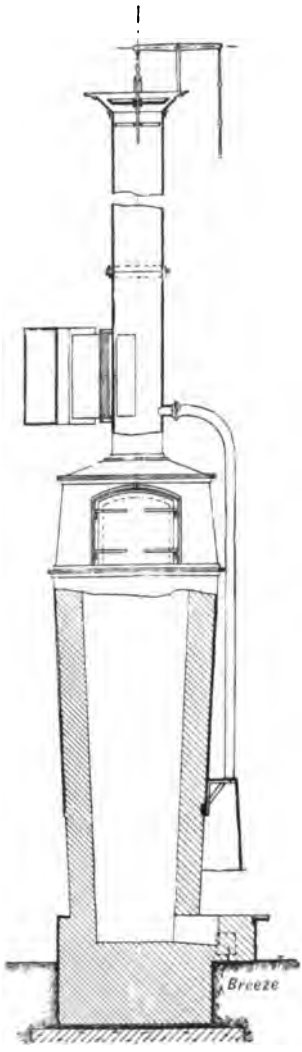
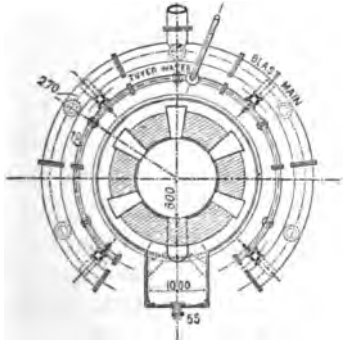


Fig. 75.

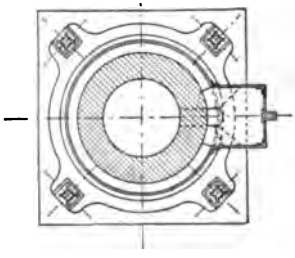
The furnace used at Oker is shown in Figs. 73 to 77. It is 19 feet 9 inches high, 4 feet in diameter at the bottom, 4 feet 3 inches at the tuyeres, and 5 feet 9 inches at the throat. It has a fixed forehearth (*sumpf-ofen*). With a blast







Foundation Plate





FIGS. 73 and 76.

FIGS. 74 and 77.

pressure of 1·4 inches of mercury it smelts in twenty-four hours 20 tons of a charge containing 11¼ tons of ore; the consumption of coke is 33 per cent. of the weight of the ore, equal to 20 per cent. of that of the charge.

The furnace used at Brixlegg in the Tyrol is 23 feet high, 5 feet 7 inches in diameter at the throat, and 4 feet at the tuyeres, and

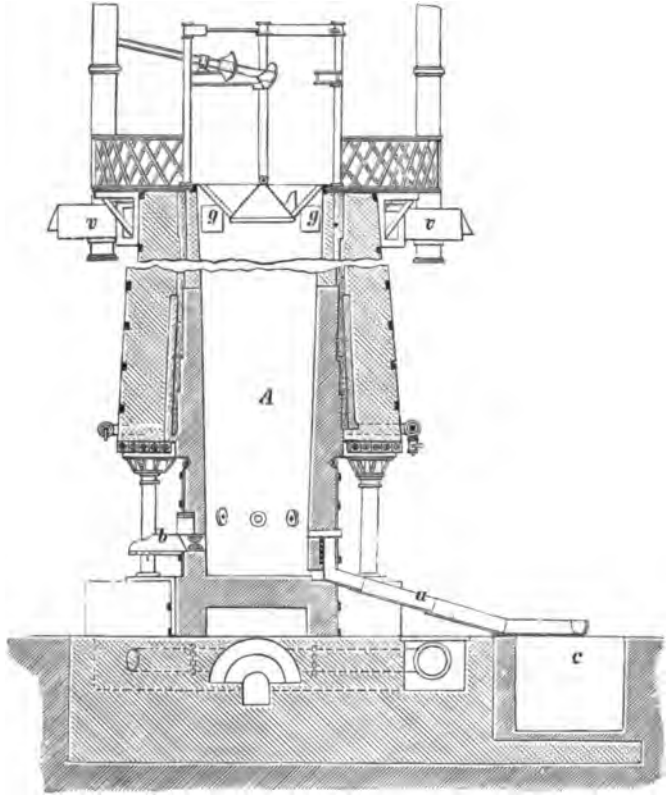


FIG. 78.

smelts in twenty-four hours 12 tons of quartzose copper ores with a coke consumption equal to 35 per cent. of the weight of the ore, and with a blast pressure of 0·8 to 0·9 inches of mercury.

The Mansfeld circular furnace is shewn in Figs. 78 and 79. It has a crucible hearth, is from 24 feet to 29 feet 6 inches high, and has from four to six tuyeres, at a height of 3 feet 7 inches above the furnace bottom. Its diameter at the tuyeres is from 5 feet 3 inches to 6 feet 2 inches, and at the throat 7 feet 3 inches. *A* is the shaft, *b* the slag

notch, out of which the slag runs through two receivers into movable slag pots. The matte tapped from the furnace runs through the gutter *a* into sandbeds; it used formerly to be granulated in the vessel *c*, which was filled with water. There are four flues at *g* to take the gases off into the downcomer *v*. When a number of furnaces are grouped together, the gases are utilised for heating the blast. The furnace is charged by means of a cone terminating in a cylinder below, which can be raised and lowered inside a hopper (modified *cup and cone*). The tuyeres and taphole are cooled by means of water.

These furnaces will put through up to 165 tons of Kupferschiefer

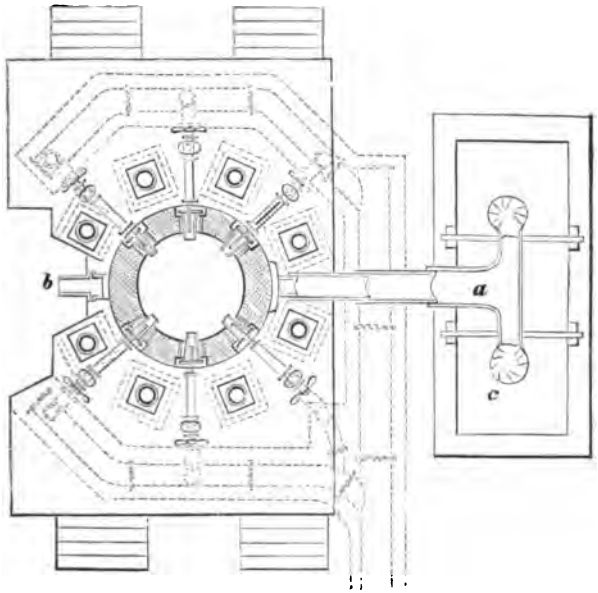


FIG. 79.

in twenty-four hours with a consumption of coke equal to 16 per cent. of the schist, the quantity smelted depending on the pressure of the blast and the area of the tuyere section of the furnace.

The water-jacket furnace is employed in the United States of North America, and is shown in Figs. 80 and 81. It has an independent, movable forehearth, into which the outlet from the furnaces opens low down. The furnace proper is made of a double casing of boiler plate, there being a space of 2 inches between the plates in which water is kept circulating. The diameter of the furnace at the tuyere level is from 3 feet 6 inches to 4 feet, the throat being from 8 to 12 inches wider. The height from tuyere to throat

is 10 feet, the bottom being from 12 to 14 inches below the tuyeres. The water-jacket is continuous down to the bottom of the furnace; the water enters near the bottom through the pipe r and escapes at the top by the pipe y. The following table, taken from Peters,[1] shows the consumption of water with furnaces running normally :—

Area of hearth square feet.	Water per hour. U.S. gallons.[2]
3	460
5	600
7	950
9·5	1,100
12·5	1,300
18	1,500
24	1,800
30	2,000
36	2,200

These figures refer to water that passes once only through the water-jacket; if the water is used over and over again the only loss should be that due to evaporation, the amount of which depends on the climate.

The bottom of the furnace consists of a dished-out plate of iron which is bolted to the lower edge of the furnace; upon this a bed of fireclay is rammed, so that the furnace bottom v is just flush with the outflow o. The furnace is supported on four columns. A blast main n surrounds the furnace, and from it the blast enters the furnace by six to eight tuyere holes u. The forehearth T, in which the molten material accumulates, is made of cast iron lined with fireclay, and is fitted with a removable cover. The lining of the bottom rests on a bed of slag. There are a taphole m for the matte and a slag notch p in the forehearth, which runs on wheels and can be pushed close up to the outflow of the furnace, a thin layer of matte or slag sealing the two firmly together. Matte and slag separate perfectly within this forehearth. In order to keep the outlet open, a minimum of 20 tons must be put through the furnace in 24 hours. Moreover, the matte may not be too rich, or it would set in the forehearth, and could not be tapped out. In time, however, the lining gets cut away. Accretions and sows are also apt to form on the walls and bottom of the forehearth, when the charge contains much iron. The forehearth must therefore be removed from time to time for repairs, but a second

[1] *Op. cit.* 1895, p. 280.

[2] One U.S. gallon = 0·83271 English gallon.

forehearth is kept in reserve, by which the damaged one can immediately be replaced so as not to interrupt the working of the furnace. When matte is tapped, the slag notch p is closed by a clay plug so that no blast can escape and cool the furnace or forehearth. The slags from this furnace contain less than $\frac{1}{2}$ per cent. of copper. K is the outlet flue for the furnace gases, which are best led through dust chambers on their way to the stack.

In such a furnace, 4 feet in diameter, with six tuyeres and a blast pressure of $\frac{5}{8}$ lb. to the square inch, 56 tons of pyritic ore with 2·8 tons of sand are put through in twenty-four hours with a consumption of coke equal to 20 per cent. of the weight of the ore.

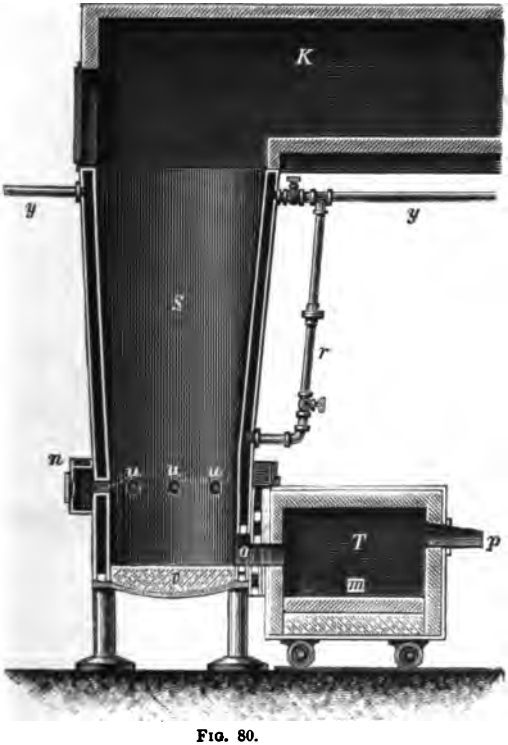


FIG. 80.

At Stratford, Vermont, a furnace 3 feet 3 inches in diameter at the tuyeres, with five tuyeres and a blast pressure of $\frac{1}{2}$ lb. to the square inch,

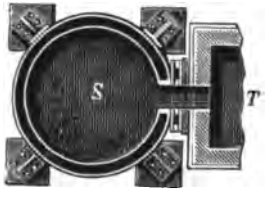


FIG. 81.

treats 40 to 45 tons of pyritic copper ore in twenty-four hours. At Phœnixville similar furnaces will handle from 35 to 50 tons of ore in twenty-four hours according to the character of the ore.

Under certain circumstances a forehearth is used heated independently by means of a lateral fireplace, so as to form a small reverberatory furnace of which the forehearth proper is the hearth; this arrangement is said to have special advantages when the matte is to be taken direct to the converter, and has been used at the Elliot metal works in South Wales, as well as in other places.

FURNACES RECTANGULAR IN CROSS-SECTION

These furnaces may be either built of brick or water-jacketed. The *Orford furnace* is a brick furnace; its construction is shown in Figs. 82 to 84. It is used at the Orford Works in New Jersey for smelting cupriferous pyrites, and is a modified or improved Raschette furnace. It is rectangular in plan with vertical walls; instead of tuyeres, there are openings in the brickwork into which the blast

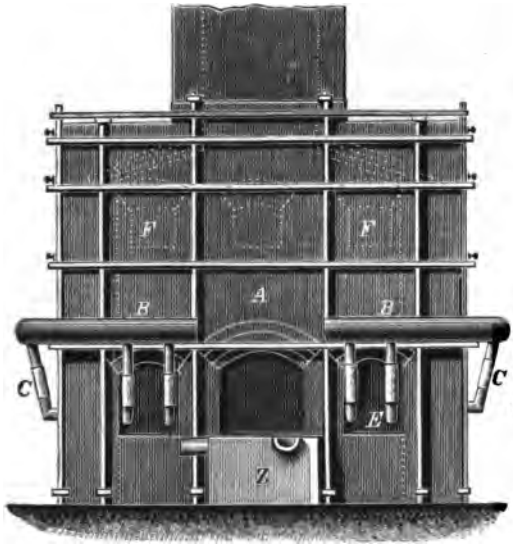


FIG. 82.

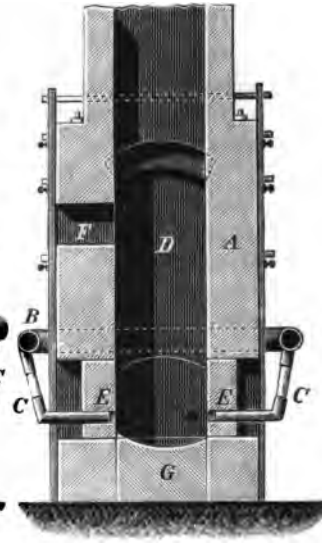


FIG. 83.

pipes project for a certain distance. It has an independent forehearth situated in the centre of one of its longer sides.

Its dimensions in plan are 3 feet 5 inches by 11 feet 8 inches inside and 8 feet 5 inches by 16 feet 8 inches outside. The height depends upon the amount of iron in the ore: for cupriferous pyrites it measures 8 feet from the level of the tuyeres to the bottom of the charging door. The bottom, which is made of firebrick, is situated up to 10 inches below the tuyeres; in the middle it slopes towards the outlet in the front side of the furnace. There are fourteen blast pipes, 6 in the rear wall, 2 in each of the short sides, and 4 in the front wall; each pair of blast pipes traverses arches through which they enter the firebrick lining. The blast pipes are connected with the blast main B by means of leather tuyere boots. As is shown in Figs. 83 and 84, the blast pipes do not go up to the

inner face of the brick lining, but only enter a short way, and are made air-tight by means of clay. The molten materials flow from the outlet of the furnace into a forehearth *z*, which is divided into two compartments communicating with each other. It is built of cast-iron plates, is 4 feet long by 3 feet 6 inches broad, and is lined with firebrick. A partition of firebrick, 9 inches thick, divides it into two compartments, a larger and a smaller, the respective areas of which are as 5 : 2. There is a low slot in this partition at the very bottom of the vessel. Each compartment has its tap-hole, *y* and *x*; that of the smaller compartment being at a lower level than that of the larger. The molten material, matte, and slag flow from the furnace into the larger compartment; by means of the manipulation already explained, matte is kept continuously flowing from the notch *y* whilst slag flows continuously from the slag-notch *x*.

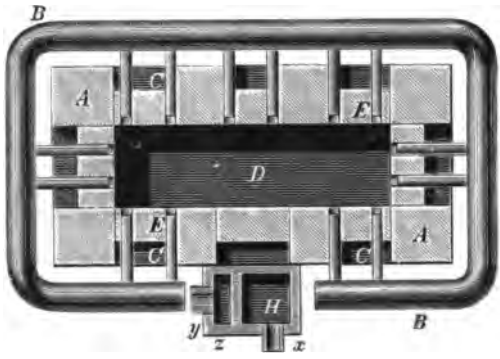


FIG. 84.

If the matte contains over 60 per cent. of copper it is apt to set on the bottom of the forehearth whilst the latter is being filled, and thus to close up the slot, whilst if it contains under 25 per cent. it rapidly cuts away the lining and cracks the cast-iron plates. Such a furnace will put through 90 to 95 tons of easily-fusible cupriferous pyrites in twenty-four hours, with a blast pressure of 0·8 inches of mercury and a coke consumption equal to 15 per cent. of the weight of the ore.

The *Henrich furnace* is a water-jacketed furnace of rectangular cross-section, which is also employed in the United States. It is shown in perspective elevation in Fig. 85. It is built up of cast-iron water jackets, has boshes and a crucible hearth. There are fourteen tuyeres, five in each of the longer and two in each of the shorter sides. Its dimensions at the tuyere level are 5 feet 6 inches by 2 feet 9 inches; the boshes commence 10 inches above this level, and are 30 inches in height, the dimensions there being 6 feet 6 inches by 3 feet 9 inches. The section of the furnace widens from this point for a height of 7 feet 6 inches to 7 feet 3 inches by 4 feet 6 inches, and then continues parallel up to the throat, which is 10 feet 6 inches above the tuyeres. The slag notch is 6 inches below

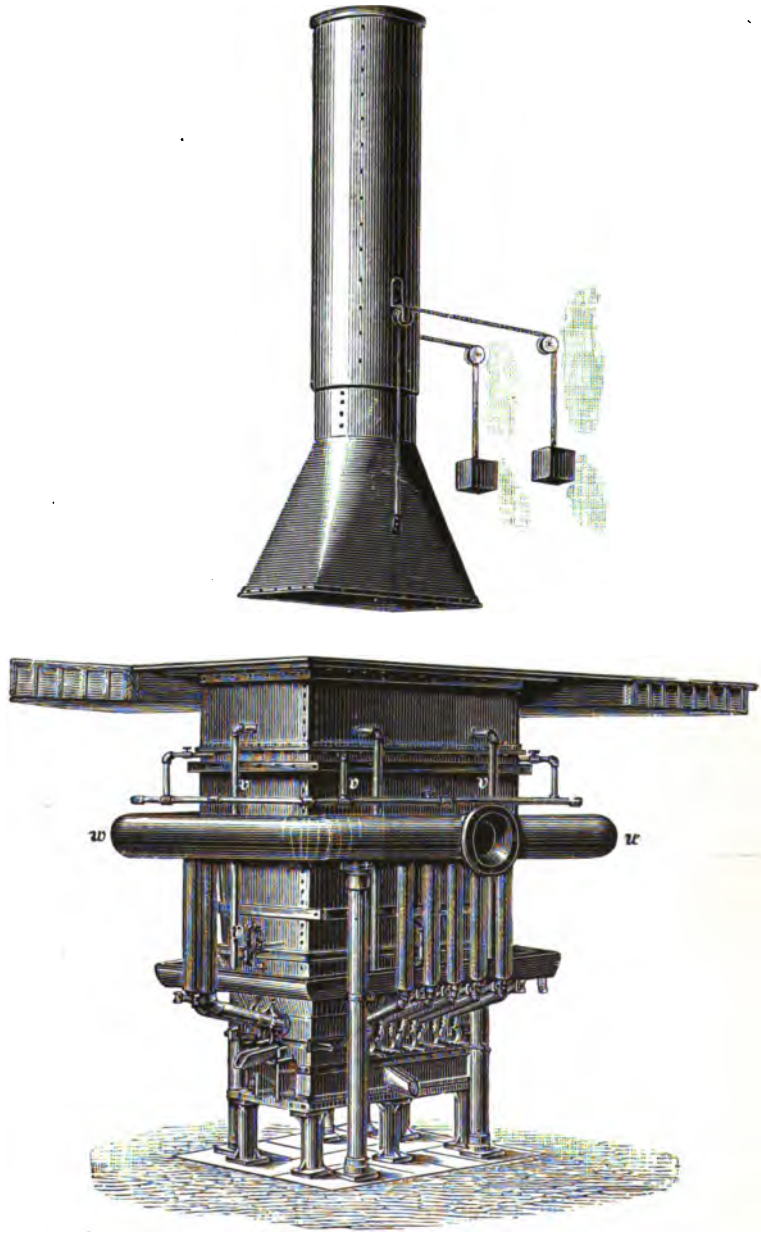


Fig. 85.

the tuyeres, and the crucible, which is lined with firebrick, is 14 inches deep. Up to the present only carbonates and oxides have been smelted in this furnace at Clifton, Arizona, where it gave very satisfactory results.

FURNACES OVAL IN CROSS SECTION

To this class belong the Skinder and the Herreshof furnaces, the former being a brick-built furnace, the latter a water jacket.

The Skinder furnace is said to have done good work at Nishni-

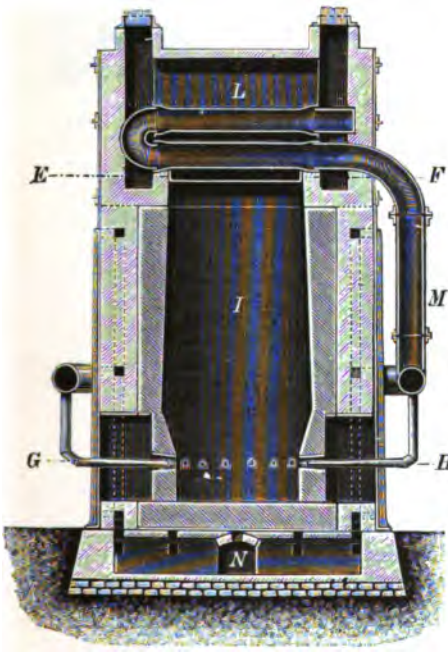


FIG. 86.

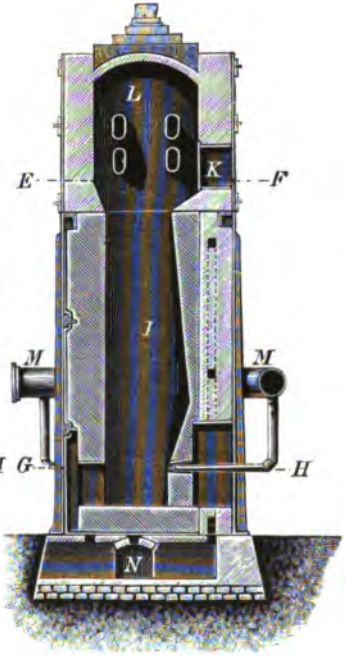


FIG. 87.

Tagilsk, in the Urals, where it is used for smelting a mixture of sulphuretted and oxidised copper ores. Figs. 86 to 89 show its construction; it has ten tuyeres, and three of its walls have boshes, the front wall being vertical. The hearth is of the crucible pattern. *K* is the charging door and *L* the blast-heating apparatus, which raises the temperature of the air to about 100° C.

The Herreshof furnace is a very large water jacket, and has been used with very good results at the Nicholson Works, near Brooklyn. It is shown in sectional elevation and plan in Figs. 90 and 91. *H* is

the water jacket, made of boiler plate, the water space being 2 inches wide. The furnace is 10 feet high from the bottom to the

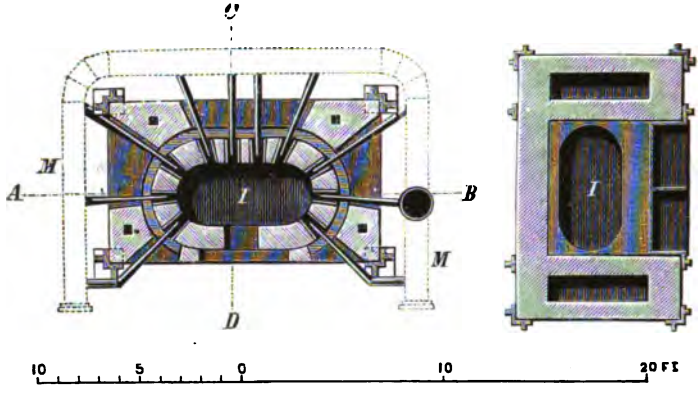


FIG. 88. FIG. 89.

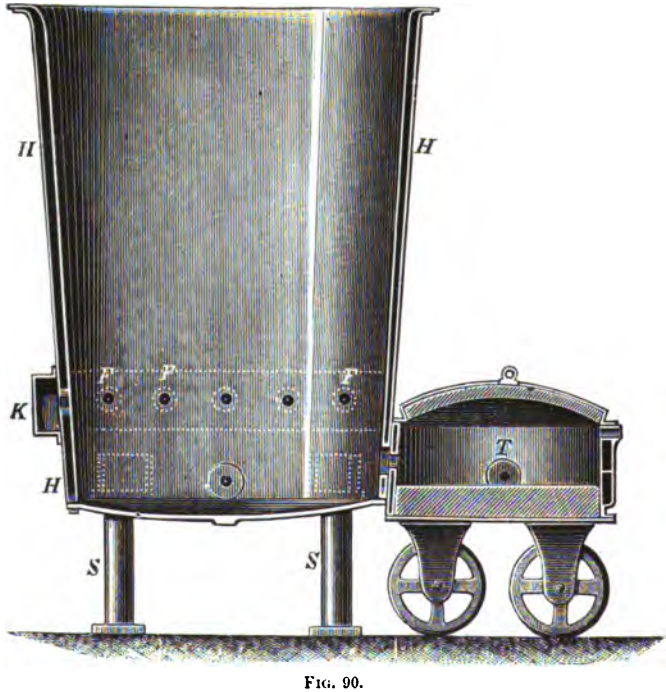


FIG. 90.

throat; its dimensions are 6 feet 4 inches by 3 feet 6 inches at the bottom, and 7 feet 3 inches by 4 feet 5 inches at the throat. The tuyeres are 26 inches above the bottom; there are thirteen tuyeres,

five in each long side and three in the rear side. *K* is the blast main. The furnace has an independent forehearth *T*, surrounded by a water jacket, with a brick-lined bottom and removable cover. The slag flows out through a slag notch near the top, whilst the matte is tapped out through a tap-hole, fitted with a bronze water block like a Lührman slag tuyere, situated close to the bottom of the forehearth. The bottom of the furnace consists of a dished iron plate bolted to the bottom edge of the water jacket. Upon this there is a thin layer of sand and then a bed of firebrick, upon which the molten matter is allowed to set solid up to the level of the furnace outlet, through which the matte and slag run into the forehearth. Whilst the furnace is in operation, the level of the molten materials is kept above the upper edge of the outlet, so that no blast can blow through



FIG. 91.

it, and with this object the slag notch is also stopped with clay during the tapping. The outlet is 9 inches high and 7 inches wide. This furnace smelts 76·8 tons of roasted cupriferous pyrites and 13·2 tons of raw smalls, equal to 90 tons of ore and 5·3 tons of sand in twenty-four hours, with a consumption of coke equal to 18 per cent. of the weight of the ore.

The forehearth must be removed from time to time and repaired, as accretions of iron and of matte form in it. A forehearth lasts from two to thirty days, according to the character of the slag and the amount of copper in the matte. In order not to stop the furnace, the forehearth, when removed, is immediately replaced by a fresh one.

THE PROCESS OF ORE SMELTING

The method of conducting the operation depends on the character of the ores, the kind of fuel, and the shape and size of the furnace.

As a rule, it should be carried on by horizontal charging and with a cold top. The weight of the charge also is variable with the conditions above-named; when charcoal was used as fuel the heaviest charge has been 3 cwt. With coke, in large furnaces, it may exceed 1 ton, and is, for instance, 1·2 tons at Mansfeld, where the Kupferschiefer is treated, and from 1·3 to 1·8 tons in the Orford furnace, running on cupriferous pyrites.

The charge, fuel ratio, quantity and pressure of blast must all be regulated so that the slag shall not contain over ½ per cent. of copper and so that no iron bears may form; as already pointed out, these latter may result from either too much or too little silica in the slag. Before any attempt is made to alter the charge, care must be taken that the real cause of the trouble is understood, as it happens at times that more silica is added to an already too siliceous mixture in the belief that the difficulty arises from too high a proportion of iron. In furnaces with independent forehearths, these troubles are far less serious with water jackets than in brick furnaces, because the brick-work of the latter is also apt to be involved, whilst there is also the danger that bears may form inside the furnace, when the latter is of the crucible or of the fixed forehearth type.

PRODUCTS OF THE FUSION

In addition to coarse matte and slags, the smelting of copper ores often produces speiss and bears of iron; when the ore is over-roasted a certain amount of black copper may also be formed. The latter is very impure, and is either resmelted in the ore or matte furnace, or, when rich in silver and gold, is treated by wet methods.

Coarse matte, which is to be roasted and smelted for coarse copper, ought to contain from 25 per cent. to 45 per cent. of copper. Formerly, in some places, *e.g.*, in Sweden, with ores rich in sulphur and insufficient roasting, mattes used to be made carrying only 8 per cent. to 12 per cent. of copper, the further treatment of which involved heavy expenses. Besides copper and iron, the matte may contain larger or smaller quantities of zinc, lead, nickel, cobalt and silver. In many mattes there is enough sulphur present to form monosulphides of the metals (except of copper, which is always present as cuprous sulphide Cu_2S), whilst in others there is so little sulphur that the metals must either be present as subsulphides or in the free state, the latter being, as already stated, the preferable view in the case of iron.

The following table shows the composition of certain mattes that were smelted direct for coarse copper :—

Localities.	Oker (old process).	Fahlun (old process).	Kedabeg in the Caucasus.
Cu	57·6—61·9	8·3—12	43·8
Fe	11·1—16·9	55·8—62·9	28·65
Zin	—	1·2— 2·9	0·257
Ni, CO	1·1— 2·1	—	1·291
Pb	0 — 1·4	0·6— 3·9	0·281
Ag	0·06	—	0·086
S	24·9—24·3	25·6—27·2	23·667

The composition of the slags has already been referred to (*see* p. 90); some of these are added to the slag charge. If they contain much copper they must be resmelted, in some cases with the addition of raw ores.

Speiss is often produced intentionally to prevent arsenic and antimony from passing into the matte : it always takes up a certain amount of the silver present. The following is the composition of two varieties :—

Locality.	Schmöllnitz.	Neusohl.
Cu	12·99	41·18
Pb	0·09	0·89
Fe	12·63	35·41
Ni	1·40	0·09
Co	0·09	0·04
Sb	60·00	10·79
As	7·42	6·10
Ag	0·36	0·03
Au	0·06	—
S	2·04	2·60
Bi	1·26	—

These speiss are worked separately to recover the copper, gold or silver that they contain.

The iron bears, sows or salamanders consist principally of metallic iron, together with copper and other metals and their compounds with sulphur, phosphorus, silicon, carbon, antimony and arsenic; the iron is produced by reduction of its oxides or by separation from mattes that were over saturated with this metal.

After suitable preparatory treatment, the copper and other valuable metals present are extracted as far as possible. With

this object the bears are broken up either by sledge-hammers or by blasting, and smelted in shaft furnaces with raw ore for matte. Or else they may be scorified (*verblasen*) or smelted in reverberatory furnaces with sulphuretted ores, or treated with acids after the matte has been liquated out from them.

The other bye products of smelting calcined copper ores, such as furnace residues, dross, skimmings, &c., when they contain copper, are added to the furnace charges, sometimes after having first been concentrated by washing.

CALCINATION OF THE MATTE

For the production of coarse copper, matte is roasted dead or sweet, that is to say, it is roasted until almost all the sulphur is got rid of; a small quantity of sulphur must be left, in order to sulphurise any copper that might otherwise pass into the slag, and to collect it in a matte. It is therefore better not to roast enough than to roast too much.

The object of this calcination is to convert copper, iron, and all other non-volatile metals into oxides, the sulphur escaping as sulphur dioxide, and arsenic and antimony being also driven off as far as possible, whilst a very small quantity of the sulphides of iron and copper remains undecomposed. The chemical reactions in matte roasting are identical with those of ore-roasting, except that the calcination is carried further. The products of the operation are a mixture of oxide of copper, peroxide and magnetic oxide of iron, and oxides of the other metals, together with small quantities of sulphates and undecomposed sulphides. The calcination can be performed in heaps, stalls, shaft furnaces, reverberatory and muffle furnaces.

Matte roasting in heaps has the disadvantages already mentioned under ore roasting. It liberates sulphurous fumes and when repeated calcinations are required, involves the lying idle of a large amount of capital; its great advantage is that the calcined matte is delivered to the smelting furnaces in lump form. It is now but rarely used and then only in districts where the sulphurous fumes can do no damage, and where sulphuric acid has no marketable value; on the other hand it is often employed as a finishing roast for mattes that have been previously calcined in shaft furnaces.

Stall roasting is no cheaper than heap roasting, requires an expensive plant and is unhealthy for the men engaged in emptying the stalls; on the other hand it presents the advantage that the injurious effect of the gases evolved may be more or less completely

neutralised by leading them into high stacks. When this is not an object, heap roasting under cover (to prevent any sulphate of copper from being leached out by rain-water) is preferable to stall roasting. The latter method also leaves the roasted matte in lump form. It too is used for the finishing roasting of matte previously roasted in shaft furnaces.

Calcination in shaft furnaces with or without previous crushing of the matte is used when the sulphurous fumes cannot be allowed to escape into the air, or are to be used in the manufacture of sulphuric acid. In this method the matte cannot be roasted sweet, nor can matte rich in copper, and apt to frit readily, be treated by it. It is not possible in this way to reduce the sulphur below 10 per cent. to 14 per cent., wherefore this mode of roasting can only be looked upon as preliminary, to be followed by a second roasting in stalls or heaps for lumps, or in reverberatory furnaces for crushed matte.

Reverberatory furnace calcination is the best for matte, as it allows of large quantities being roasted sweet in the shortest possible time. Its disadvantages are a high consumption of fuel, the necessity of crushing the ore, which has then to be smelted in the form of powder, and the impossibility of utilising the gases evolved; on the other hand they can be led into high stacks and thus rendered less destructive. It should always be employed when the possibility of utilising the gases is prevented by the absence of a market for sulphuric acid, by the matte being too rich in copper, or the gases produced being too poor in sulphur. It should be used as a finishing roasting for crushed mattes, that have already been calcined in shaft or in muffle furnaces, as also for similarly treated lump ores in cases where the latter are not to be roasted in heaps or stalls, with the object of saving time, and when it is preferred to carry off the sulphurous gases in reverberatory furnace stacks, rather than in the stacks of roasting stalls; such lumps must however, first be crushed before they can be roasted in the reverberatory furnace.

Muffle furnaces admit of the sulphurous gases being employed in sulphuric acid manufacture, but are only suited to crushed matte, and entail a comparatively high consumption of fuel. They are therefore, but rarely used in matte roasting.

Dead-roasting of matte in heaps

This is best carried out under shelter to prevent the sulphate of copper being leached out by rain-water. The process is the same as in the case of ores except that, on account of the lower contents of sulphur and greater richness in copper of the matte, the heaps must

be smaller, and the calcination several times repeated, generally from two to six times according to the nature of the matte, in the case of mattes containing much arsenic and antimony as often as twelve times. The heaps may vary in size from 50 to 150 tons of matte. For the first roasts the heaps are made lower and longer than for the latter ones, in order to diminish as far as possible the inevitable melting together of the matte just above the fuel bed. For the subsequent roasts, when the quantity of sulphur is less, the quantity of wood in the bed must be increased, and the heaps made shorter and higher. Layers of charcoal or of chips of wood are then also introduced in order to destroy the sulphates, arseniates and antimoniates that may have been formed during the calcination.

In the United States the preference is given to heaps containing 60 to 70 tons of matte, 12 feet square and 6 feet high; the practice of piling the heap round a small chimney in order to regulate the draught is also recommended. Whilst the author was at Kedabeg in the Caucasus, heaps holding 100 tons were in use there. At the Stephanshütte in Upper Hungary, the heaps averaged 56 to 84 tons capacity, 1 foot 4 inches high for the first roast, and 8 feet to 9 feet high for the tenth to the thirteenth roasts; for the fifth to the seventh roasts, charcoal was mixed with the matte.

The time occupied depends on the nature of the matte; the first roast takes 8 to 14 days, the subsequent ones less time. The general average may be taken to be from 6 to 8 weeks for dead roasting. During the first roast, kernels will often be found to form in the lumps of matte.

Well roasted matte has a bluish-black colour, is porous, sintered and often shows metallic copper separated out in the interior of the lumps in consequence of the interaction of cuprous oxide upon sulphide of copper left undecomposed.

The consumption of wood is very variable and depends on the character of the matte, on its contents of sulphur, arsenic and antimony, and on the number of calcinations required. According to Peters, in the United States 60 tons of matte require three cords of wood for each roast. At the Stephanshütte 50 tons of matte, which had to be calcined 12 to 14 times on account of its high proportion of antimony, required 459 cubic feet of wood and 318 cubic feet of charcoal. In the Caucasus 17 to 20 tons of matte required two cubic fathoms of wood.

Dead roasting of matte in heaps, which is now rarely employed, was in use in Sweden, Norway, Russia, the Upper and Lower Harz, Hungary, and America.

Dead Roasting of Mattes in Stalls

This is a more rapid process than the last, but is now seldom used, as it has generally been replaced by calcination in reverberatory furnaces.

In the United States (Boston, Vermont), stalls are in use that are provided with a brick arched roof and a fire grate, and having the following dimensions: Width 5 feet, length from the back to the front wall (which latter has to be built up every time the stall is filled) 6 feet, height from the grate to the spring of the arch 4 feet 8 inches, height from the floor to the grate 1 foot 6 inches. Flues for the escape of the gases are constructed in the rear wall. A bed of wood is laid on the grate and upon it from 5 to 6 tons of matte are piled. The first roast usually takes four days, the following ones three days. For each charge from 10 to 20 cubic feet of wood, according to the character of the matte, are consumed; hard wood is far more effective than soft.

Heine[1] has recommended for matte roasting stalls 6 feet square and 5 feet high, which were to take 10 tons of matte for the first calcinations and 5 to 6 tons for the later ones.

Calcination in Shaft Furnaces

These furnaces are used for the preliminary roasting of mattes, the sulphurous gases from which it is proposed to utilise; to remove the sulphur completely a finishing roast must be given in heaps, stalls, or reverberatory furnaces.

For matte in lump form, kilns, as previously described, see p. 49, are employed. Mattes containing over 50 per cent. of copper are too readily fusible to be suitable for kiln roasting. Pyrites burners are not high enough to be suitable for calcining mattes. In order to prevent the lumps from fritting, more or less roasted matte is mixed with the raw matte, according to the fusibility of the latter. By this addition it is possible to prevent accretions forming in the furnace, but its capacity as regards raw matte is of course proportionately diminished. At Altenau, in the Harz, furnaces 4 feet 9 inches wide, 5 feet 8 inches long, and 9 feet 2 inches high will put through 1·25 tons of matte (0·75 tons raw and 0·5 tons roasted) in twenty-four hours. In the modern kilns at Oker which are 13 feet high, 4 feet wide, and 7 feet 6 inches long (whereas the old ones were 13 feet high, 4 feet 6 inches wide, by 8 feet long), 3 tons of matte containing

[1] *Bergmannsfreund*, i. 51.

32 to 39 per cent. of copper, 20 to 30 per cent. being calcined matte, are treated in twenty-four hours. After this roasting at least three other roasts are required to roast it dead, as calcination in the shaft furnace only brings the sulphur down to between 8 and 10 per cent.

For crushed mattes the Gerstenhöfer furnace is the only one that has been used. The matte on being tapped is granulated and then ground. The objection to this furnace is the great amount of flue dust that it produces; in one of them at Mansfeld (where they were used at one time, but were taken down on account of the just named objection) 10 to 15 tons of coarse matte could be roasted from 25 to 29 per cent. of sulphur down to 12 to 14 per cent. Of course this calcination had to be followed by a dead roasting in reverberatories. No other form of shaft furnace has yet been tried, nor are these likely to give satisfactory results, seeing how apt the matte is to frit together.

Calcination in Reverberatory Furnaces

This is the best and most convenient method for roasting matte. Any of the already described furnaces may be employed, but their stacks should be as lofty as possible. As the matte contains less sulphur than the ores, more fuel will be required for its calcination and the output of the furnaces will be less.

At Altenau in the Oberharz 3½ to 4 tons of matte are roasted from 20 per cent. down to 2 per cent. of sulphur in twenty-four hours in a hand-worked long-bedded reverberatory (*Fortschaufelungsofen*), with a consumption of coal equal to 20 per cent. of the weight of the matte.

At Brixlegg, in a similar furnace, 3 tons are roasted dead in twenty-four hours, with a consumption of 46 cubic feet of peat to the ton of matte.

In Omaha, Nebraska, 6 tons of matte are roasted from 35 per cent. down to 3 per cent. of sulphur per twenty-four hours in a Brückner furnace, with a consumption of 1 ton of coal.

It is a difficult matter to roast dead in continuous-acting rotating cylinders, unless the matte is made to pass through a series of these.

Calcination in Muffle Furnaces

This is very rarely used, and would only be indicated when sulphurous fumes cannot be allowed to escape into the air. The Hasenclever muffle furnace would probably be the best adapted to this purpose. The author knows of no instances where muffle furnaces are at present employed for the dead roasting of matte.

SMELTING THE ROASTED MATTE FOR COARSE COPPER

Dead roasted matte consists essentially of oxides of copper and iron with small quantities of sulphates and undecomposed sulphides. By smelting in shaft furnaces the oxide of copper is reduced to metal and the oxide of iron to ferrous oxide, which is slagged off. Any copper sulphate present would be split up, leaving oxide of copper, which is also reduced. A part of the sulphides of copper and iron is decomposed by the oxides of copper, forming metallic copper and ferrous oxide, which latter passes into the slag; another part must remain undecomposed so that the sulphide of iron may react with any silicate of copper that may have been formed producing silicate of iron and sulphide of copper, the latter combining with the remaining undecomposed sulphides to form a rich matte (*dünnstein*); it is the production of this matte that saves the copper from being slagged off.

In order to slag the iron, acid slags from ore smelting, slags from fining or refining copper, or better still oxidised copper ores, containing quartz or acid silicates, are added to the charge in such quantities as to form a monosilicate slag.

The same furnaces are used as for ore smelting; they must not be too high or the reducing action of the carbon monoxide would be too great, so that ferriferous copper and bears of metallic iron would result. Charcoal tends to produce a purer copper than does coke.

In order to prevent the formation of bears inside the furnace, and to prevent the matte absorbing metallic copper (which it does if left long in contact with it), the furnace is usually supplied with independent forehearths, and has two outflow apertures or "eyes" (*Brillen-ofen*). Besides the objections just named, there is danger, with the two other forms of hearth, of the metallic copper chilling in the tap hole.

The blast pressures varies between 0·6 and 1·2 inches of mercury. A furnace, according to its size, will put through from 6 to 15 tons of calcined matte in twenty-four hours with a fuel-consumption of between 15 per cent. and 25 per cent. When the furnace with two "eyes" is used, the fused materials are allowed to run alternately through each into the forehearths or wells, in which the coarse copper and matte collect and separate according to their specific gravities, whilst the slag flows over the lips of the forehearths. Whilst the one "eye" of the furnace is stopped, the corresponding well is emptied, by first cooling the surface of the matte and lifting it off in thin layers and then similarly taking off the coarse copper in discs. A coarse copper

smelting campaign lasts a shorter time than a matte smelting campaign, because bears of iron form, and the brickwork of the furnace is rapidly attacked by the highly basic slag.

Coarse copper or *black copper* contains, according to the purity of the matte, from 70 to 99 per cent. of copper. The coarse copper produced in American works is fairly pure as shown by the subjoined partial analyses :—

	Ely pig copper.	Ore Knob pig copper.
Iron . .	1·1 to 1·6 per cent.	. . 1·4 per cent.
Sulphur .	0·7 to 0·8 „	. . 1·1 „
Copper .	98·4 to 97·2 „	. . 96·8 „

The composition of various European black coppers is as follows :—

	Mansfeld.	Fahlun (Sweden).	Atvidaberg (Sweden).	Stefanshütte (Upper Hungary).
Cu	94·52	94·44	94·39	86·50
Fe	0·62	3·29	2·04	3·50
Zn	1·09	0·33	1·55	—
Pb	1·93	0·57	0·19	—
Ag	0·03	0·07	0·11	0·25
Ni	0·76	0·23	0·63	trace
Co	0·23	0·18	—	trace
S	0·86	0·75	0·80	1·05
Sb	—	—	—	8·46

Black copper cannot, on account of the impurities it contains, be used as such in the arts, but has first to be purified. If, as is often the case, it contains a considerable proportion of silver, the latter is recovered by means of dry, wet or electrical methods (treatment with lead, amalgamation, lixiviation or electrolysis).

The rich matte (*dünnstein* = "thin matte," so called because it is removed in thin discs from the black copper over which it collects) is a matte containing up to 70 per cent. or more of copper. It is a combination of cuprous sulphide (Cu_2S) with ferrous sulphide (FeS), and is full of vesicular cavities in which metallic copper is found in mosslike or hairlike forms. According to Plattner, a matte consisting of Cu_2S and FeS has the property, when molten, of dissolving metallic copper with the formation of Cu_2S and Fe_2S; when slowly cooled, the metallic copper separates out, and FeS is again formed. Metallic silver is also found in mattes rich in silver, the formation of which is explained in the same way, Ag_2S and Fe_2S being formed at high temperatures, and metallic silver and FeS on cooling. According to Münster, the copper in the matte is reduced in consequence of a

reaction between the cuprous oxide (in the slag) and cuprous sulphide. The sulphur dioxide thus formed is said to drive the metallic copper out of the matte at the moment of its solidification.

This matte is, like the coarse matte, roasted sweet and smelted for coarse copper. The composition of *dünnstein* is shown by the following analyses :—

	Mansfeld.	Fahlun.	Phönixhütte (Upper Hungary).
Cu	70·89	59·75	60·00
Fe	5·63	13·82	16·52
S	20·95	21·96	22·25
Zn	0·52	1·00	—
Pb	0·60	4·08	—
Ag	0·01	—	—

The slags are generally monosilicates, sometimes, however, containing rather more silica than is required by the above ratio. They always contain certain quantities of copper (1 to 3 per cent. of cuprous oxide), and are therefore added to the charge in the ore furnace, where their high contents of ferrous oxide is available for slagging siliceous matter.

The following table shows the composition of such slags :—

	Mansfeld.	Fahlun (Sweden.)	Röros (Norway).
Silica	29·94	30·93	31·44
Ferrous oxide	45·14	69·07	55·21
Alumina	7·31	—	7·86
Lime	5·77	—	—
Magnesia	1·25	—	4·46
Cuprous oxide	2·42	not determined	—
Zinc oxide	5·45	—	—

At Mansfeld, 10 to 12 tons of calcined matte used formerly to be smelted in twenty-four hours in a *brillenofen* 19 feet 5 inches high, with one tuyere, with a consumption of coke of 25 per cent.

At Brixlegg, dead roasted matte with 15 per cent. of quartz and 15 per cent. of ore-furnace slag is smelted in a furnace of the *Pilz* pattern, 23 feet high, 4 feet diameter at the tuyeres, and 5 feet 7 inches at the throat, with a blast pressure equal to 0·6 inches of mercury. A mixture of coke and charcoal is used as fuel. This furnace treats 8 tons of matte in twenty-four hours.

At Kedabeg, furnaces, 16 feet 5 inches high by 4 feet 3 inches by

5 feet 7 inches, smelted in twenty-four hours, 6 to 7 tons of dead-roasted matte, with a consumption of charcoal of 50 per cent. of the weight of the matte.

At Altenau, in the Upper Harz, furnaces with two "eyes" (*Brillenöfen*) and one tuyere, from 11 feet 10 inches to 15 feet 10 inches high and 3 feet 3 inches in diameter, smelted 5 tons of dead-roasted matte, with variable amounts of slag in twenty-four hours, with a blast pressure of 0·8 inches of mercury and a consumption of 1½ tons of coke.

At Atvidaberg and Fahlun in Sweden, where black copper used to be produced by smelting dead-roasted matte, the dry method has been replaced by a wet method of copper extraction. The furnaces were similar to the previously-described *Sulu-furnaces*, but were narrower, 16 feet 10 inches in height, and had a crucible hearth. The charge consisted of 2 parts (by weight) of roasted matte, 0·20 to 0·40 parts of ore furnace slag, 0·20 to 0·40 parts of cupriferous residues (refinery dross) and, under some circumstances, a certain quantity of quartz. The consumption of coke was 0·6 parts to 2 parts of roasted matte.

The German Process of Copper Extraction Combined with the Concentration of Matte

This process, as already mentioned, is made use of when the coarse matte is poor in copper, or is contaminated by notable quantities of arsenic and antimony or lead. The first matte is then only roasted to a definite point, and is then smelted to produce a purer matte, richer in copper than the first, in which any silver present will also be concentrated.

If this matte (known as *spurstein*, answering about to "blue metal") is impure, containing As, Sb or Pb, its calcination to a definite degree followed by a smelting of the matte thus calcined, may be repeated one or more times. This process is spoken of as a second, third, &c., *spuren*, ("concentrating" or "doubling"). The results of these operations are mattes of high purity, rich in sulphide of copper or silver, together with slags.

The calcination of matte to a definite degree is effected in the same manner and with the same plant as have already been described, but it is not carried as far as dead-roasting. In many cases, however, it is carried so far that together with matte a certain quantity of black copper is obtained, which takes up antimony and arsenic, together with a great part of the silver-contents, and especially the gold-contents of the matte.

The roasted matte is smelted in the same furnaces as are used for ore and for black copper smelting. In order to slag off the iron, additions are made to the charge, of acid slags from the ore furnace, quartzose copper ores, or ores mixed with acid silicates, in such proportions that a mono-silicate slag results. These slags always retain over ½ per cent. of copper, and are added to the ore furnace charge.

Concentration in shaft furnaces has in most works been replaced by concentration in reverberatories, because purer mattes are obtained in the latter. On the contrary, mattes rich in lead, and which yield lead on smelting, are more advantageously treated in shaft than in reverberatory furnaces. This is the case with lead-bearing copper mattes, as also with the mattes produced in treating leady copper ores, such as the so-called mixed ores at Oker. For example, at Oker, by the smelting in shaft furnaces of ores containing 4·78 per cent. copper, 8·84 per cent. lead, 12·55 per cent. iron, and 24·11 per cent. sulphur, which are first calcined in shaft furnaces down to 10 to 12 per cent. of sulphur, and then by two heap roastings brought down to 5 to 6 per cent., the products obtained are work-lead, and a matte with 16 to 20 per cent. copper, 4 to 5 per cent. lead, and 0·02 per cent. silver. This matte is then roasted in shaft furnaces, and smelted in shaft furnaces with the addition of siliceous copper ore, known as *Kniest*, forming matte with 45 per cent. copper, and 0·05 to 0·06 per cent. silver, and an alloy of copper, lead, arsenic and antimony, containing up to 60 per cent. of copper.

The composition of various of these mattes (*spursteine*) as formerly produced is shown in the following table :—

	Freiberg.	Altenau.	Mansfeld.	Oker.
Cu	32—43	63·9	51·37	64·38
Fe	16—20	8·1	18·67	8·93
Pb	14—17	7·3	—	2·95
Ni, Co, Zn	—	—	6·54	1·34
Ag	0·2—0·3	—	—	—
S	21—24	20	24·35	20·79

When the *spurstein* is rich in copper it shows segregations of metallic copper like the *dünnstein*, already referred to.

The composition of the slags made in this process is shown by the analyses on the following page :—

	Mansfeld (older slags.)	Altenau.	Oker.
Silica	33·1—34·1	27·6	27·14
Alumina	5·6—11·2	6·5	17·82
Ferrous oxide	32 —51·5	54·3	47·93
Lime	5 —17·1	4·1	3·41
Magnesia	0 — 4·6	0·6	—
Cuprous oxide	0·7— 3·0	1·4	—
Lead oxide	—	4·8	—
Antimony oxide	—	1·0	—
Sulphur	0 — 0·46	—	—
Zinc oxide	—	—	1·24

The capacity of the furnaces, blast pressure and fuel consumption are similar to what they are when dead roasted matte is smelted.

At Oker, matte containing 35 to 45 per cent. of copper used to be first roasted in kilns down to 10 to 11 per cent. of sulphur, which was further brought down to 4 to 5 per cent. by two calcinations in heaps; it was then smelted in shaft furnaces with two tuyeres, of 9 feet in height from the tuyeres to the throat, with the addition of 20 to 30 per cent. of *kniest* (clay-slate containing copper pyrites) with a blast pressure equal to 1 inch of mercury, the products being *spurstein* and black copper. In 24 hours 7 to 8 tons of matte were smelted with a consumption of coke equal to 38 to 40 per cent. of the charge.

At Altenau in the Upper Harz mattes containing 25 to 40 per cent. of copper and 9 to 14 per cent. of lead are roasted in the furnaces already described (*see* page 115) from 20 down to 7 per cent. of copper. The roasted matte is smelted in round shaft furnaces 3 feet 3 inches in diameter with two "eyes" and one tuyere, yielding a concentrated matte with 70 per cent. of copper and a certain amount of coarse copper. With each 100 parts of matte, 140 parts of slags are charged; the blast pressure is equal to 0·6 to 0·8 inches of mercury. In 24 hours 5 tons of matte are smelted with the consumption of 1½ tons of coke.

Examples of the German Process of Copper Smelting

The German process is still carried on in but few places, as the matte-concentration and the fusion for black copper are generally performed in reverberatory furnaces, so that a combined Anglo-German process results.

It is, for example, still used at Brixlegg for copper ores free from silver, these consisting of quartzose copper pyrites with 15 per cent.

of copper. They are in part roasted in heaps, in parts smelted raw; whilst the author was in Brixlegg, it was proposed to replace heap roasting by roasting in long reverberatory furnaces.

The ores, 25 per cent. roasted and 75 per cent. raw are, on account of the amount of silica they contain (27 per cent.), mixed with lime and basic slags and smelted in *Pilz* furnaces. These furnaces are 23 feet high, 5 feet 7 inches in diameter at the throat, and 4 feet at the tuyeres, and their hearth is protected by cast iron water boxes. The blast pressure is equal to 0·8 to 0·87 inches of mercury. In 24 hours 12 tons of ore are smelted with a consumption of coke equal to 35 per cent. of the weight of the ore. The coarse matte (*rohstein*) thus produced contains 35 per cent. of copper. The slag containing 0·15 to 0·4 per cent. of copper is in part thrown away and in part added to the charge for coarse-copper smelting.

The matte is granulated and calcined sweet in reverberatory furnaces; these latter are long furnaces with two hearths and are heated by peat-gas. Such a furnace holds altogether 3 tons of matte, which is roasted dead in 24 hours with a consumption of 46 cubic feet of peat to the ton of matte. The dead-roasted matte is smelted, with the addition of 15 per cent. quartz and 15 per cent. ore-furnace slag, for black copper, in furnaces with two "eyes." The blast pressure is 0·6 inches of mercury, and 8 tons of matte are smelted in 24 hours. The products are black copper, *dünnstein* and slag; the first-named is refined, the second treated like the ordinary matte and the slag added to the ore-furnace charge.

At Kedabeg, ores were treated containing pyrites, quarz and zinc blende. The lump ore was roasted in heaps, the fines in Gerstenhöfer calciners, and then smelted with charcoal for coarse matte. The latter, containing 10 to 30 per cent. of copper was dead roasted in heaps and then smelted for black copper and *dünnstein;* the latter was roasted dead and also smelted for black copper.

At Atvidaberg, ores carrying quartz and blende were formerly roasted once in heaps and stalls, ores carrying pyrites twice. In order to get rid of the zinc, two layers of charcoal were interposed in the ore; the first roasting lasted 4 to 6 weeks, the second one for the pyritic ores 3 to 4 weeks. At first the sulphide of zinc was only imperfectly decomposed, so that on smelting the ore, a mixture of sulphides and slag containing up to 8 per cent. of copper known as *skumnas*, was obtained, the further treatment of which was attended with difficulties. Later on, by means of a better conducted calcination, by which the sulphide of zinc was converted into oxide, the formation of this *skumnas* was prevented. The roasted ores were smelted in the

previously described *sulu-furnaces* with the addition of slags from the ore-furnace and the coarse-copper furnace, producing coarse matte with 25 to 30 per cent. of copper and a bisilicate slag. The consumption of fuel was 60 per cent. of charcoal or 30 per cent. of coke.

The coarse matte was roasted in stalls 4 or 6 times in the space of 6 to 8 weeks, charcoal being mixed with it in the last calcinations, and it was then smelted in shaft-furnaces with fixed forehearths with the addition of ore slags and refinery residues, producing black copper and *dünnstein*, which latter was mixed with the coarse mattes in the final calcinations. The fuel used was coke and its consumption in smelting was 30 per cent. of the weight of the calcined matte.

The copper ores at Fahlun were treated by the same process as that just described.

At Agordo in the Venetian Alps, kernels from kernel roasting, containing 7 to 8 per cent. of copper, were formerly smelted raw with rich pyrites and with cement copper obtained by leaching the crusts with water, and precipitating the solution with iron, with the addition of slags and sandstone, in furnaces with two "eyes," 18 feet in height. The coarse matte thus produced was roasted dead and was smelted with roasted *dünnstein*, ore-furnace slags, rich slags and sandstone, in furnaces with fixed forehearths, 14 feet 9 inches in height, producing black copper and *dünnstein*.

At Stefanshütte, in the district of Zips, Upper Hungary, 60 per cent. of roasted and 40 per cent. of raw fahlore, containing 14·5 per cent of copper and 0·06 per cent of silver is smelted with the addition of coarse-copper slags and quartz, in a shaft furnace, 8 feet 6 inches high by 3 feet 3 inches wide with 3 tuyeres. The products are coarse matte with 30 per cent. of copper and a cupriferous speiss, the consumption of fuel (charcoal) being 25 per cent. of the weight of the ore. The coarse matte is roasted 12 to 14 times in heaps, and then smelted in shaft furnaces for black copper and *dünnstein*.

As an example of the German process with matte concentration, Mühlbach in the Salzburg district may be quoted. The works have now however been removed, and are now conducted on the Anglo-German method at Bischofshofen in the Salzach Valley.

At Mühlbach the ore, consisting of copper pyrites, quartz, arsenical pyrites and spathic ore, and containing a small amount of nickel, was smelted raw with the addition of ore-furnace and coarse-copper slags and some roasted coarse matte, so that the charge contained on the average 13 per cent. of copper. The furnace used was a round shaft furnace 16 feet 5 inches high, with crucible hearth and five tuyeres, the blast pressure being 0·55 inches of mercury, and the product a

coarse matte with 23 per cent. of copper. This was twice roasted in stalls and then smelted in a two "eyed" furnace with two tuyeres, with a blast pressure of 0·47 inches of mercury, together with 10 per cent. of quartz and 10 to 20 per cent. of ore-furnace slag, producing a concentrated matte with 55 to 60 per cent. of copper and a small amount of black copper. This second matte was crushed between rolls and roasted in a long reverberatory furnace, which produced 1·8 tons of dead roasted matte in 24 hours with a consumption of 247 cubic feet of wood. The dead roasted second matte was smelted in a *brillenofen* with the addition of ore-furnace slag and quartzose sand, producing black copper and *dünnstein;* the latter was ground and added to the charge for black-copper smelting.

The English Process of Copper Smelting

As already explained, the English process depends upon the reaction of the sulphides of iron and copper with the oxides of copper; the reduction of the latter is therefore brought about, not by carbon as in the German process, but by the sulphur of the above named sulphides. The carbon or fuel in the English process serves only for the production of a temperature sufficient for the above reactions, whilst in the German process it acts both as fuel and as a reducing agent.

The English process differs from the method of lead reduction by calcination and reaction, in that the copper is not obtained like lead by a single calcination and smelting operation, but that a whole series of operations are required, and that with the exception of the roasting for coarse copper, the calcinations are conducted in separate furnaces from the smelting.

In its simplest form the reverberatory furnace method embraces the following operations:—

1. The calcination of the ore.
2. Smelting the calcined ores in reverberatory furnaces for *coarse metal.*
3. Calcination of the coarse metal.
4. Smelting the calcined coarse metal in reverberatory furnaces for *fine metal* or *white metal.*
5. Treating the fine metal in reverberatory furnaces for coarse copper or *blister copper,* either after previous calcination or direct, the latter being the so-called *roasting.* English copper smelters restrict the word *roasting* to this particular operation, and do not use it as synonymous with calcining, as is generally the case.

The smelting process may in the rare case of very pure and rich ores, be simplified by roasting the coarse metal direct for blister copper, and thus omitting the concentration stage. Very often, on the other hand, the process is modified by the protraction of the concentration stages, particularly when the object is to obtain copper of high quality from varied mixtures of impure ores. With ores containing arsenic, antimony and tin, as also when they are auriferous, the concentration processes are so conducted as to produce a certain quantity of coarse copper, known as *bottoms*, in which the gold, tin, antimony and arsenic are collected; the matte produced at the same time as the bottoms, sometimes called *spongy metal*, is comparatively pure and is suitable for the production of the better grades of copper. This is known as the *best-selecting* process. From the *bottoms* so obtained, only inferior copper can be got by dry methods, but the better grades can be produced from them by electrolytic operations.

The prolongation of the concentration operations, *i.e*, the production of various grades of matte (*metal*) and coarse copper is especially practised in England, where, as at Swansea in South Wales, and St. Helens near Liverpool, the most varied classes of foreign ores with impurities of all kinds are treated. A somewhat complicated process of reverberatory furnace smelting has thus originated in Swansea for the treatment of these ores, spoken of as the "Welsh" process, which will form the subject of a special description.

In recent times the reverberatory has often been combined with the shaft-furnace process, the ore smelting, and sometimes the smelting for black copper, being performed in the latter.

The Simple English Process

(*Without repeated concentration operations*)

CALCINING THE ORES

The object of the calcination of the ore is the partial removal of sulphur, whilst the metals originally combined with it are converted into oxides; at the same time so much sulphur is to be left in the ores, that on fusion a part of the iron, as well as the whole of the copper remains combined with sulphur. If it is required to produce on smelting a slag containing less than $\frac{1}{2}$ per cent. of copper, the matte or metal must not contain much over 35 per cent. of copper. In places, however, where the ores are relatively rich and pure, whilst labour and fuel are costly, *e.g.*, in

Montana, it is found more economical to calcine more thoroughly so as to produce a richer matte with 60 per cent. of copper, and to leave over 1 per cent. of copper in the slags. The following table drawn up by Peters, shows the proportion of copper in the slags with varying proportions of copper in the mattes, as produced in the Parrot Works in Butte, Montana :—

Percentage of copper in the matte.	Percentage of copper in the slag.
64·3	0·85
62·7	1·05
66·5	0·92
66·2	1·10
65·9	0·67
61·8	0·64
63·6	0·87
64·5	0·82
63·3	0·76
66·2	1·32

For the reason given above, at the Anaconda Works, Montana, a matte with 60 per cent. of copper is produced, in Chili with 50 per cent., at the Wallaroo Works, Australia, with 50 to 55 per cent.

The chemical reactions during calcination are the same as those in the German process; whilst all that has been said regarding the furnaces employed in the latter process applies equally to the former.

The English calciners proper have been of late years replaced by long reverberatories with hand or power rabbling, by the rotating cylinders of Brückner and Oxland, and by shaft furnaces for the purposes of sulphuric acid making.

The older type of English calciner is shown in Figs. 92 to 94. In these x is the grate, lying 5 feet below the roof and 3 feet 4 inches below the fire bridge; it is often worked with a so-called clinker bed; h is the bed 30 feet long and 12 feet wide, 1 foot below the roof at the flue bridge, and 4 feet at the fire bridge; c are openings through which the roasted ore is emptied into four vaults situated beneath the furnace; these vaults communicate with flues through which the gases evolved are led away; y is the fire bridge, d a *curtain* arch to preserve the ore at the bridge end from too strong a heat; a are openings through which the ore is charged from the hoppers m. These are kept closed during the calcination by slabs of firebrick or by slides. At n are shown the working doors on both of the longer sides for rabbling the ore; in order to enable the latter to be reached on every part of the hearth, the walls of the

furnace are built with obtuse projections on the inside; *b* is the flue, leading to the culvert *c* resting on iron girders. In many furnaces, there is a channel through the entire length of the firebridge, which communicates by three openings with the interior of the laboratory or calcining space; through this hollow firebridge, known from its inventor as Sheffield's firebridge, cold air can enter from outside, and

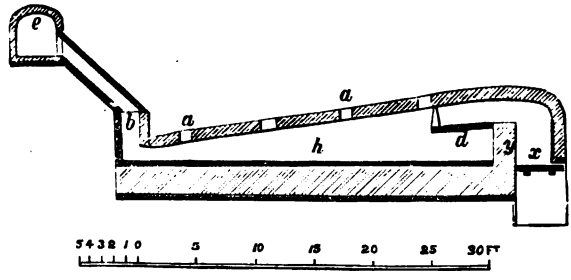


FIG. 92.

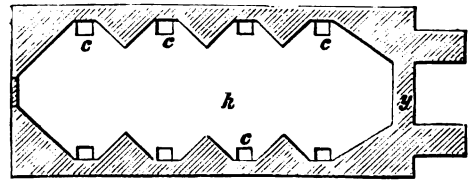


FIG. 93.

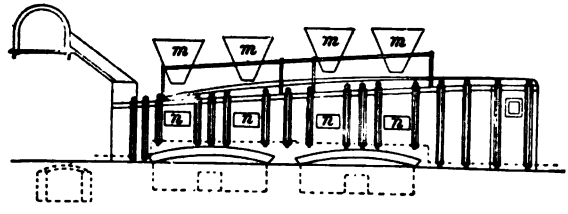


FIG. 94.

is thus heated, whilst at the same time keeping the bridge cool. In such a furnace 7 tons of ore can be roasted in twenty-four hours. The consumption of coal is said to be from 12 to 15 per cent. of the weight of the ore, but is probably higher.

As explained under the German process, the modern long continuous furnaces, and rotating cylinders can put through considerably more ore, and hence are often used in the English process, unless the gases evolved are to be used in sulphuric acid making.

Intermittently worked furnaces offer the advantage that the charge can be introduced whilst red-hot into the smelting furnace, as is done with Brückner furnaces at Anaconda, Montana, thus causing a considerable saving of time and fuel.

In order to utilise the gases for making sulphuric acid, the muffle furnaces of Spence have been used in England; they are either fired by an independent grate or heated by the waste heat of the smelting furnaces.

Such a muffle furnace heated by waste heat is shown in Fig. 95. *S* is the smelting furnace, *M* the muffle which is heated from below by the gases from the smelter passing into the chamber *r* and thence through the flue *k* into the stack. The ores are charged from the hopper *t* at the upper end of the muffle and drawn forward from time

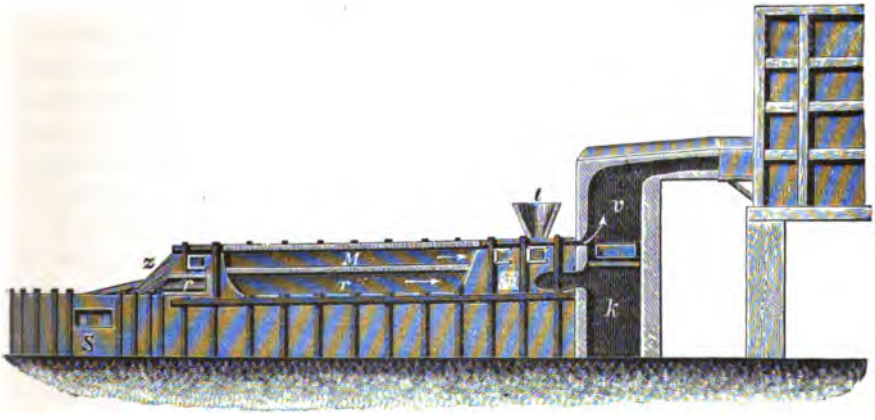


FIG. 95.

to time to its lower end, whence they finally drop through the flue *z* into the smelting furnace *S*. Ths gases evolved during calcination escape through the flue *v* which leads to the sulphuric acid chambers. It is said that such a furnace will roast 6 tons of ore in 24 hours. This arrangement is open to the objection that calcination and smelting are completely dependent on each other.

Ore intended to be used for sulphuric acid making, which is too fusible to be calcined in shaft furnaces, would probably be best calcined in the previously described Hasenclever furnace.

SMELTING THE CALCINED ORE FOR COARSE METAL IN REVERBERATORY FURNACES

The calcined ores consist chiefly of oxides and sulphides of iron and copper, and contain subordinate quantities of sulphates. The

oxides and sulphates of copper are to be converted into sulphide, and to combine with the undecomposed sulphide of copper and sulphide of iron to form a regulus or matte, known as *coarse metal;* the ferric oxide is to be reduced to the ferrous state and slagged off together with the earths, silicates and quartz present in the ore, and the oxides of any of the heavy metals, except copper and the precious metals, that may be present. The slag should contain so much silica as to be intermediate between a mono- and a bi-silicate.

The various kinds of ores available are so mixed that no large amount of fluxes may be required; otherwise too great quantities of slag would be formed, which would cause heavy losses of copper. To quartzose ores slags from the fine-metal furnace and the roasting furnace are added, whilst pyritic ores are mixed with others rich in quartz. According to the character of the ores, the amount of slag to be added may amount to 30 per cent. of the weight of the ore.

As soon as a sufficient temperature is reached in the smelting furnace, the oxides commence to react, as also do the sulphates (that have not already been split up into oxides with evolution of sulphur dioxide and oxygen) with the sulphides present, forming metallic copper, cuprous or cupric oxides as shown in the following equations :—

$$Cu_2S + 2CuO = 4Cu + SO_2$$
$$Cu_2S + 2Cu_2O = 6Cu + SO_2$$
$$Cu_2S + 3CuO = 3Cu + Cu_2O + SO_2$$
$$Cu_2S + 6CuO = 4Cu_2O + SO_2$$
$$Cu_2S + CuSO_4 = 3Cu + 2SO_2$$
$$Cu_2S + 4CuSO_4 = 6CuO + 5SO_2$$

The metallic copper thus formed deprives the sulphide of iron of a portion of its sulphur, forming cuprous sulphide, thus :—

$$2Cu + 2FeS = Cu_2S + FeS + Fe \text{ (or } Fe_2S)$$

The oxides of copper formed as above react with fresh portions of undecomposed sulphide of copper.

Another portion of the oxides of copper reacts with sulphide of iron in the presence of silica, forming cuprous sulphide and ferrous oxide, which latter at once combines with silica to form ferrous silicate, thus :—

$$FeS + Cu_2O + xSiO_2 = Cu_2S + FeO + xSiO_2$$
$$4FeS + 6CuO + xSiO_2 = 3Cu_2S + 4FeO + xSiO_2 + SO_2.$$

This sulphide of copper unites with the sulphides of iron and copper remaining undecomposed to form coarse metal.

The ferric oxide contained in the roast ore can only be slagged

off as ferrous oxide; it is reduced to the lower stage of oxidation by the sulphur of the sulphide of iron, which latter in the presence of silica removes so much oxygen from the ferrous oxide as to reduce it to the ferrous state, being itself oxidised to sulphur dioxide, as in the annexed equation:—

$$FeS + 3Fe_2O_3 + xSiO_2 = 7FeOxSiO_2 + SO_2.$$

It is also possible that a portion of the ferric oxide may be reduced by the metallic iron, produced as shown above, to the ferrous state and so slagged off, thus:—

$$Fe_2O_3 + Fe + xSiO_2 = 3FeO + xSiO_2.$$

Of the remaining constituents, arseniates and antimoniates are in part reduced by sulphides to the metallic state, and pass into the matte and in part decomposed by silica. Sulphide of zinc goes partly into the matte, partly into the slag; sulphide of lead goes into the matte, as does all the silver present. Oxide of zinc goes into the slag.

If the ores are over calcined, raw ores are added, if not calcined enough, oxidised ores are added to the ore-furnace charge.

The smelting furnace or *smelter* has an oval concave bed, made of sand, crushed sandstone or quartz; the sea-sand used for this purpose in Swansea consists according to Percy of:—

Silica	87·87 per cent.
Alumina	2·13 ,,
Oxide of iron	2·72 ,,
Lime	3·79 ,,
Magnesia	0·21 ,,
Carbon dioxide and water	2·60 ,,

The crushed quartz used for this same purpose in Montana, contains, according to Peters, from 95·3 to 97·2 per cent. of silica. The bed is usually put on in several layers; the bottom layer consists of a material that either contains sufficient base naturally, or to which sufficient slag is added, to cause it to frit. This is put on in one layer and heated until it commences to sinter, or if the material is more difficultly fusible it is put on in several layers which are fritted together one at a time, until they finally form an impenetrable mass. The upper layer, or the true bed, is also put in one or more layers.

In Wales, for instance, the bed is formed of a layer of sand 8 to 10½ inches deep over which a certain quantity of slag is scattered,

and strongly heated. Upon this two thinner layers of sand are then fritted. The average thickness of the bed is 20 inches; it generally rests upon a bed of clay.

The older English smelters were rather small, not being able to take a bigger charge than $1\frac{1}{2}$ tons at one time. In the United States these furnaces have been made much larger, so as to be capable of taking a charge of 6 to 7 tons, and quite recently (1894) up to about 11 tons[1] (25,000 lbs.), without either the time or the fuel required being increased in anything like the same proportions. The older beds were 13 feet 6 inches long by 9 feet broad, but afterwards they were made 15 feet by 10 feet; more recently, at Argo, Colorado, these dimensions were increased to 22 feet by 14 feet, and

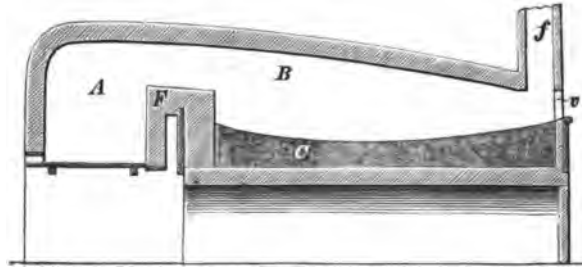


FIG. 96.

ultimately in 1894 to 35 feet by 16 feet; at the same time instead of narrowing gradually from its widest part near the middle to the fluebridge, the sides are now brought in abruptly, so that the area of the modern hearth is far greater than that of the older type. The construction of the older English smelting furnace, the so-called Welsh furnace, is shown in Figs. 96 to 99. It is 13 feet 4 inches long and 9 feet wide. Experience has shown that in these small furnaces, the best area for the bed is 154 square feet and for the fire-place 17 to 19 square feet. *A* is the fire-place, with fire-door *a*; *F* is the hollow fire-bridge open to the ashpit, supported by a cast-iron bridge-plate. *B* is the furnace body, *C* the bed or hearth made of sand; *f* is an inclined flue leading into the stack *E*. The charge is introduced through an opening in the furnace roof over which stands the charging hopper *M*; some slags are also charged through the working door *v*; *S* is the tap hole for tapping out the matte, which is run either into sand-moulds or into a granulator, situated in front of the furnace. The slags are drawn out through the

[1] *The Mineral Industry*, New York, 1895, p. 237.

working door v before the matte is tapped. The height of the furnace arch over the bed is 35½ inches at the fire-bridge and 16 inches at the flue-bridge. The stack is 66 feet high.

In such a furnace, charges of 1·3 tons at a time are worked off in

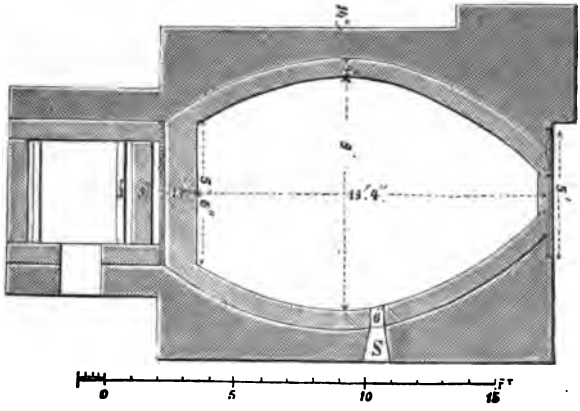


FIG. 97.

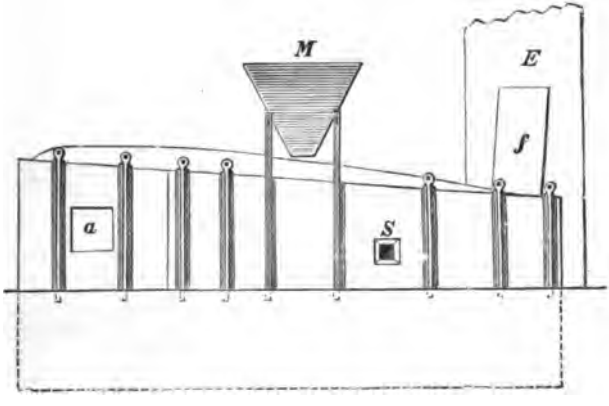


FIG. 98.

England in 3 to 4 hours; three charges are smelted in a 12 hour shift.

The construction of an American reverberatory of the newer type is shown in Figs. 100 to 104. The hearth is 22 feet by 14 feet in the clear, and the fire-place is 4 feet long by 5 feet wide, the areas being about 230 square feet and 20 square feet respectively. H is the hearth, e the fire-place, d the fire-door, c the taphole for matte, a a sort of working-door, b a tap-hole for slag, h the

working-door proper through which slag can also be drawn out, *v* the mouth of the flue, which communicates by a rising flue *k* with the stack *f*; *p* is the fire-bridge, open below. The air required for combustion enters below the grate through flues in the brick-work

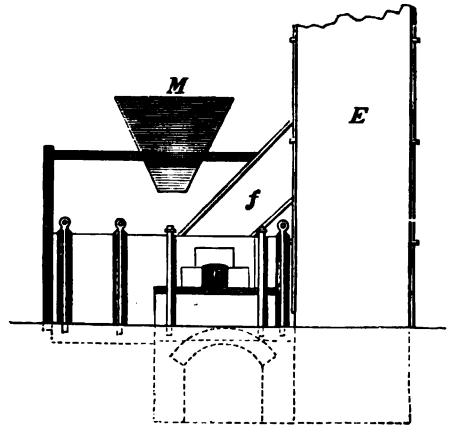


Fig. 99.

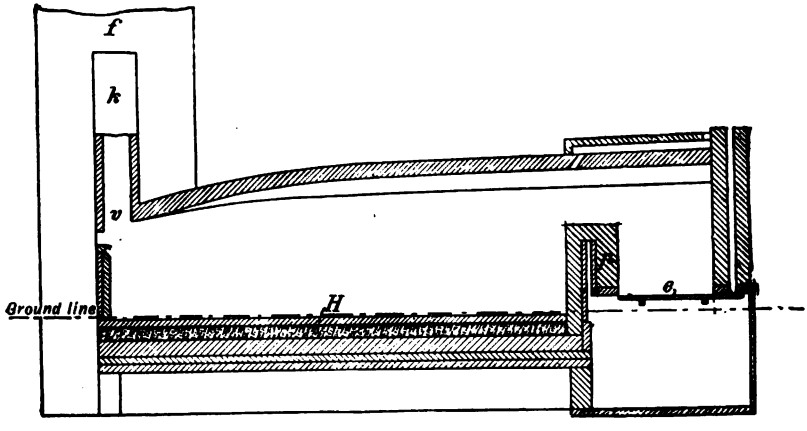


Fig. 100.

of the furnace. The slag runs into slag pots set in front of the furnace, in which any matte that may be carried over settles down, and from the slag pots it runs through cast-iron gutters to the outside of the smelting house either into slag tubs on wheels or into a stream of water, that carries it to a suitable depositing ground. If the quantity of slag is very great, as for instance at Argo, where 16 to

18 tons of slag are produced to the ton of matte, a cast-iron conical pot is fixed in front of the working door *h*, which is connected by means of a cast-iron gutter with a cast-iron collecting pot, in which the slags from the working door and the slag tap-hole collect, and

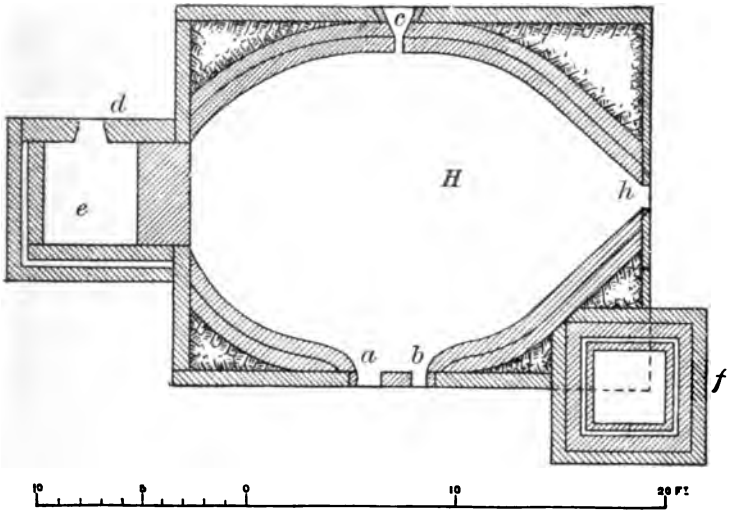


FIG. 101.

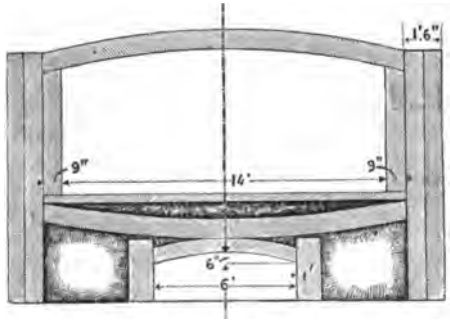


FIG. 102.

whence they flow through another gutter to the outside of the smelting house. This arrangement is shown in Fig. 105; *a* is the slag-pot, *b* the pot in front of the working door of the furnace. The slag runs through the gutters *f* and *e* into the collecting pot *c*, and escapes through the gutter *d*. The matte is tapped through the tap-hole *c* Figs. 101, 104, into sand beds or cast-iron moulds. The

ore is charged through two openings in the arch by means of hoppers.

Such a furnace puts through 28 tons of charge in 24 hours. In

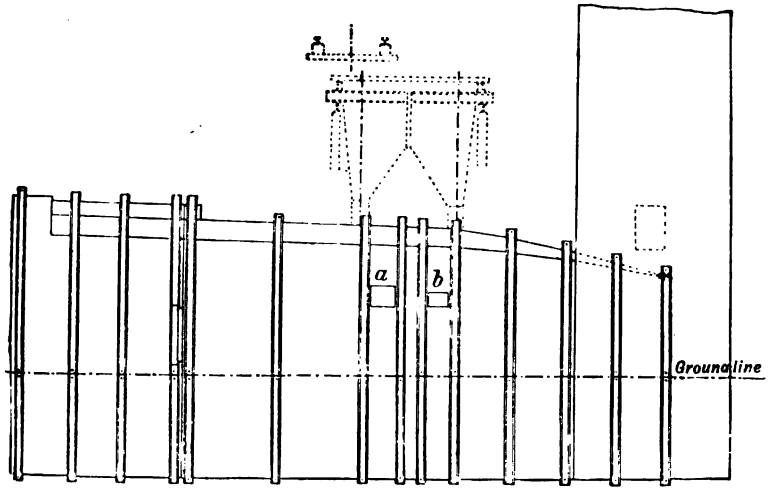


FIG 103.

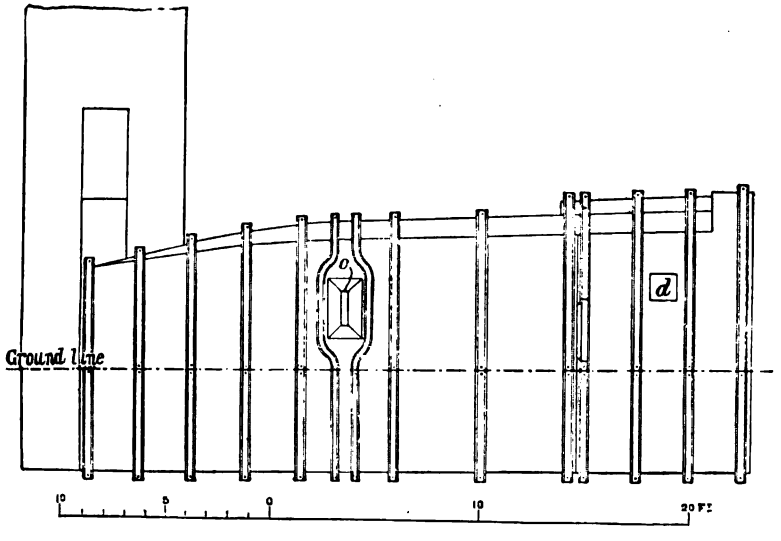


FIG. 104.

the 1894 Argo furnaces above referred to, with a hearth area of 481 square feet, a fire-grate area of 32·5 square feet, and a stack area of 16 square feet, 50 tons of ore, half hot calcined ore and half raw ore,

are smelted in 24 hours with a consumption of 13½ tons of coal (*loc. cit.*).

The process is conducted in the same manner in both large and small furnaces. The ore is dropped from the hoppers on to the bed and spread out over it. In England larger masses of slag are charged through a working door, a method that is not however to be recommended. The doors are then closed and a strong fire put on. As soon as the mass has melted down (which takes place in a few hours up to 5 hours, according to the size of the charge and to whether the ore was delivered red hot from the calciners or not) a great number of bubbles of sulphur dioxide rise up through it in consequence of the reaction between the sulphides and oxides. The mass is now rabbled through so that all parts may be thoroughly melted. As soon as the formation of bubbles has ceased, the mass is again rabbled, and then again fired strongly for half an hour to allow the matte to separate from the slag. By means of iron hooks the slag is then drawn through the working-door, or in the case of the larger furnaces, through several doors, and is allowed to run into slag pots or sand-beds, opening one into the other. In either the pots or the beds, as the case may be, any prills of matte carried over with the slag may be deposited. The matte is only tapped off after every second or third charge; as soon as the slag has been drawn out, a fresh lot of ore is dropped on to the bed, and the process is repeated as above. After two or three charges have been worked off, the matte is tapped out into a granulator, into sand-beds or into iron moulds. A certain sump of fluid matte is, however, always left in the furnace, so that no accretion may form upon the bed. For this reason and for the sake of rapid working, it is advisable to tap the matte at the longest possible intervals of times. The matte run into sand-beds is crushed or, as is done at times in England, again melted and then granulated.

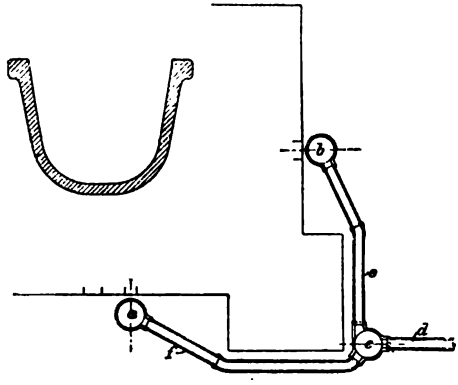


FIG. 105.

The capacity of the smelting furnaces depends upon their size and the size of the charge they can take, upon the character of the ores and fuels, and upon the ores being charged cold or red hot.

The consumption of fuel depends upon its nature, and on that of the ores, as also on the temperature at which the latter are charged and on the dimensions of the furnace.

In the small English furnace some five charges of 1·3 tons each are worked off in twenty-four hours; the fuel used is a mixture of soft coal and anthracite slack, and its consumption is 40 to 45 per cent. of the weight of the charge.

At Argo, in the furnaces above described with 6 to 7 ton charges, 20 to 30 tons are smelted in twenty-four hours with a fuel consumption of 33 per cent., coal being used.

At the Wallaroo Works in South Australia, 3 ton charges of ¾ calcined and ¼ raw ores are worked off in 6 hours. A furnace puts through 12 tons in 24 hours with a coal consumption of 49 per cent. At the Butte and Montana Works at Butte, Montana, the charge is 4½ tons of calcined ore. In 24 hours, six charges equal to 27 tons are smelted with the consumption of 10 tons of coal = 37 per cent.

At the Anaconda works, Montana, the calcined ore is transferred red hot from Brückner cylinders into the 6 ton smelters. In twenty-four hours, as was witnessed by the author at the Anaconda works, 9 charges of 6 tons each were smelted with a consumption of 9 tons of coal = 16 to 17 per cent.

The results of the ore fusion are coarse metal and slag. The percentage of copper in the coarse metal depends upon the richness of the ore in copper and the degree to which calcination had been carried.

In the Welsh process the calcination is so conducted as to produce a matte with not more than 35 per cent. of copper; this matte is known in England as coarse metal or regulus. An average sample taken by Le Play from fifty-eight separate samples had the following composition :—

Cu	33·7
Fe	33·6
Ni, Co, Mn	1·0
Sn	0·7
As	0·3
S	29·2
Slag	1·1

The slag is a mono-silicate, or is intermediate between a mono- and a bi-silicate. It always contains considerable quantities of

quartz mechanically enclosed. An average sample prepared from fifty-eight separate samples, had according to Le Play the following composition :—

Mechanically enclosed quartz	30·5 per cent.
Chemically combined silica	30 „
Ferrous oxide	28·5 „
Alumina	2·9 „
Lime	2·0 „
Magnesia	0·6 „
Manganous oxide, nickel oxide, Cobalt oxide, tin oxide	1·4 „
Calcium	1·1 „
Fluorine	1·0 „
Copper	0·5 „
Iron	0·9 „
Sulphur	0·6 „

or :—

Quartz	30·5 per cent.
Slag	65·4 „
Metal	2·0 „
Fluorspar	2·1 „

Calcination of Coarse Metal

The object of calcining the coarse metal is to remove a certain proportion of sulphur from it, the quantity to be got rid of depending on whether only a concentrated matte (*white metal*) or coarse copper is to be the product of the next smelting operation. If the former is required, the calcination is carried so far that a matte with from 60 to 75 per cent. of copper will be formed ; if the latter, the calcination is either carried so far that the calcined coarse metal shall contain oxygen and sulphur in such proportions as to produce coarse copper when smelted, or else in the smelting process a suitable proportion of raw metal is mixed with the highly calcined coarse metal. In the Welsh process the coarse metal is calcined till its sulphur contents are reduced from 30 to 13 per cent.

The chemical reactions involved are the same, and the same apparatus is used, as in the German process of matte calcination.

If it is required to either utilise or render innocuous the gaseous products of calcination, kilns are employed for lump matte, and Gerstenhöfer or Hasenclever furnaces for pulverulent matte. Other-

wise, reverberatories worked by hand or by machinery, especially long-bedded calciners, and rotating cylinders like those of Brückner and Oxland are used.

The older Welsh furnaces for metal calcination are similar to the ore calciners above described. The coarse metal is granulated, or crushed by rolls or stamps, and charged in 3½ to 5 ton charges, the heat being gradually raised to a bright redness with frequent rabbling of the charge; the temperature may not however be high enough to cause the metal to sinter or melt. The process takes twenty-four hours, and the fuel consumption is 40 to 45 per cent. of the weight of the coarse metal. The other furnaces named above give far superior results to these as regards both capacity and economy of fuel, so that they are to be used in preference to the older type.

At the Wallaroo works, a continuous acting rotating cylinder will treat 12 tons of matte in twenty-four hours with a coal consumption of 15 per cent.

At Omaha, Nebraska, a Brückner furnace calcines 6 tons of matte from 35 per cent. down to 3 per cent. of sulphur in twenty-four hours with a coal consumption of 25 per cent.

In long-bedded calciners worked by hand, from 5 to 12 tons of matte, according to the size of the furnace, can be calcined in twenty-four hours with a coal consumption of 20 to 35 per cent.

SMELTING THE CALCINED COARSE METAL FOR WHITE METAL

This operation is performed in reverberatory furnaces similar to those used in ore smelting; the chemical reactions involved are also the same. In order to slag off the iron, quartzose ores or quartz should be added to the charge. By the addition of oxidised ores, it is possible to obtain rich matte from comparatively poor coarse metal (with about 30 per cent. of copper).

The charge is first spread over the bed, and the fire is gradually increased to a white heat. After the formation of bubbles, caused by the reaction of the sulphides with the oxides, has ceased, the matte and slag separate into two layers. The slag, however, still contains cuprous oxide, which can only be transferred to the matte by long contact with the latter at an increased temperature, a corresponding amount of iron passing from the matte into the slag as silicate. The production of a slag as poor as possible in copper can therefore be brought about by increasing the heat and prolonging the operation of smelting. Thus, according to experiments of Le

Play, in smelting calcined coarse metal for white metal, the following results were obtained :—

	Percentage of Copper in the Matte.	Percentage of Copper in the Slag.
After 3 hours 10 minutes	54	9
„ 5 „	65	5
„ 5 „ 50 „	74	3·5

The matte is tapped in from 5 to 10 hours, according to the size of the charge which may vary from 1¼ to 6 tons. Matte and slag are either tapped out together into cast-iron pots or separately; in the latter case, the matte is usually run out first, and the slag which follows it, run into separate receptacles.

In England, a rich matte with 75 per cent. of copper, the so-called *white metal* is produced in the Welsh furnace by smelting calcined coarse metal with 30 to 35 per cent. of copper. For this purpose it is mixed with a due proportion of oxidised compounds, such as carbonate of copper, cuprite (red oxide), or slags rich in copper, which shall act upon the undecomposed sulphides of the coarse metal. According to Le Play, the charge weighs about 1¾ tons, and the operation is complete in 5 to 6 hours. First the matte and then the slag are tapped off into sandbeds. In 24 hours four charges, equal to 7 tons, are worked off with a consumption of fuel of rather over 50 per cent. of the charge; the fuel used is a mixture of anthracite and soft coal. Each 100 parts of the charge yield 40·2 parts of white metal, 28·1 parts rich slag, and 26·1 parts of poor slag. The average amount of copper in a fortnight's production of white metal was 73·2 per cent. The slags are mixtures of mono- and bi-silicates, containing over 2 per cent. of copper, chiefly as mechanically intermingled matte.

The composition of the rich and poor slags produced in smelting for white metal (*metal slags*), is shown by the following analyses :—

	Rich Slag.	Poor Slag.
Silica	33·0	33·8
Ferrous oxide	55·0	56·0
Cuprous oxide	2·7	0·9
Other metallic oxides	2·0	2·1
Alumina	1·6	1·5
Lime	1·4	1·4
Magnesia	0·3	0·3
Copper	2·9	2·9
Iron	0·3	0·3
Sulphur	0·8	0·8

The slags are added to the ore furnace and metal furnace charges.

At Oker, in the lower Harz, coarse metal containing 30 to 34 per cent. of copper, is calcined in kilns and smelted for white metal, containing 60 to 65 per cent. of copper. The bed of the smelting furnace is 14 feet 1 inch long by 9 feet 10 inches wide; the distance between the upper edge of the firebridge and the roof is 18½ inches; its height above the grate is 26 inches, and above the bed 15 inches; the firebridge is 28 inches broad. The firebox is 3 feet 7 inches long, 3 feet 3 inches broad, and 4 feet 1 inch high. The bed is composed of 9 parts of stamped quartz and 1 part of ground refinery slags; the height of the stack is 43 feet, there being a separate stack to each furnace. The charge consists of 2½ tons calcined matte, ¼ ton raw matte, and ¼ ton of *kniest*. The charge is dropped on to the hearth from two hoppers and spread out on it; it is melted in four hours, and the evolution of gas bubbles is practically finished in five to six hours. It is then rabbled, and slag and metal are tapped off together into 8 cast-iron pots, arranged stepwise, one below the other. The metal collects in the upper pots, whilst in the lower pots the slag and matte separate into two layers, the matte forming the lower portion. Before the contents of the pots set, a hook is inserted into each, by means of which the mass when set is lifted on to a truck and allowed to cool, after which the regulus is separated from the slag. The process lasts eight hours. In twenty-four hours 9 tons are put through with a coal consumption of 55 per cent. The matte produced contains 60 to 65 per cent. of copper, 9 per cent. iron, and 14 per cent. sulphur, whilst the slag is a mono-silicate with 2 to 3 per cent. of copper.

At Mansfeld, coarse metal, with about 40 per cent. of copper, calcined in kilns, is smelted for white metal with 70 to 75 per cent. of copper. The bed is 13 feet 11 inches long, 3 feet 9 inches wide at the firebridge, 9 feet 9 inches in the middle, and 18½ inches at the flue-bridge. It is made by smelting a mixture of quartz and ore furnace slag upon a bed of sifted quartz, 8 inches deep. The firebridge is 3 feet wide, the fire space above it being 6 inches high. The grate is 4 feet square worked with a clinker bed. The stack is 115 feet high. The charge is 3 tons of calcined coarse metal with 3·3 to 4 per cent. of quartz or highly siliceous copper ore (sand-ore from Sangerhausen). The charge is melted in five to five and a-half hours, its fusion being promoted by repeated rabbling. It is tapped one to one and a-half hours later. The matte which runs out first is allowed to run through an iron gutter lined with clay on to an iron plate; as soon as slag begins to flow with it, it is turned into a series

of five or six cast-iron pots, arranged stepwise, one below the other, in which the matte may settle to the bottom. The contents of these pots are dealt with as at Oker. In twenty-four hours 9 tons of calcined coarse metal are smelted with a coal consumption of 45 to 50 per cent. of the weight of the calcined matte.

By calcining the matte more strongly in kilns, that is, by re-calcining a portion of it, some of it goes to form *bottoms*, together with white metal containing 79 per cent. of copper and a high proportion of silver; the whole of the gold and a part of the silver passes into the bottoms.

SMELTING THE WHITE METAL IN REVERBERATORY FURNACES FOR COARSE COPPER

This can be done in two ways, namely, with or without previous calcination of the white metal. The latter is a typical English process known as *roasting*, in which the oxidation of a portion of the sulphides which is necessary for the reaction, takes place within the reverberatory smelting furnace.

SMELTING WHITE METAL FOR COARSE COPPER AFTER PREVIOUS CALCINATION

The calcination is effected in reverberatory furnaces, heaps or stalls. Shaft furnaces cannot well be used on account of the richness of the matte in copper and its correspondingly ready fusibility, together with its poorness in sulphur.

The calcined matte is smelted in the same furnaces as are used for ore smelting and metal smelting.

At Oker the white metal containing

Copper . . .	60 to 65	per cent.
Silver . . .	0·06	„
Iron . . .	9	„
Sulphur . . .	14	„

is calcined three or four times in heaps, until the sulphur is brought down to 4 or 5 per cent.; each heap contains 90 to 100 tons, and consumes 353 cubic feet of cord-wood. The first fire lasts three weeks, the second two, and the third one week.

The furnace charge consists of 4½ tons of calcined matte, together with a certain quantity—up to ½ ton—of copper refinery slags; it is all melted in six to seven hours. The fire is then urged for two hours more, and the first slag is drawn off. Another strong fire is put on,

and slag is drawn off for the second time, after which the coarse copper is tapped out. The process lasts twelve hours; the coal consumption is 55 to 57 per cent. of the weight of the calcined matte. The products are 43 to 48 per cent. of black copper containing 92 to 95 per cent. of metal, 2 to 3 per cent. of concentrated matte, slags from the first drawing with 5 to 6 per cent. of copper, and slags from the second drawing with 20 to 25 per cent.

At Wallaroo, where the matte is calcined in continuous-acting rotating cylinders, the calcined matte is mixed for smelting with a certain quantity of raw matte, the products being coarse copper and a certain amount of matte rich in copper.

In Bischofshofen, Salzburg, calcined white metal mixed with raw metal was formerly smelted in reverberatory furnaces for coarse copper.

SMELTING WHITE METAL FOR COARSE COPPER WITHOUT CALCINATION (ROASTING)

This roasting operation is peculiar to the Welsh process, and consists in alternate oxidations and reductions several time repeated, in reverberatory furnaces. By a very slow softening and subsequent drop by drop fusion of the metal with access of air, a certain amount of the copper of the matte is oxidised, and on the temperature being raised, this oxide reacts upon the sulphide remaining undecomposed. The slag produced is skimmed off, and the oxidation is repeated by allowing the molten material to cool with access of air, after which the air supply is cut off and the temperature again raised, when fresh reaction of the oxides upon the sulphides ensues.

In England, white metal, a matte with 5 to 10 per cent. of iron and small quantities of zinc, tin, cobalt, nickel, arsenic and antimony, is more particularly subjected to this process. It is carried out in furnaces similar to the ore-smelters, provided with Sheffield's hollow fire bridges. The construction of the furnace is shown in Figs. 106 and 107. In these *a* is the fire door, *z* the fire-bridge, into which air enters by the channel *b*, rises up through it, and after being thus heated, finds its way into the furnace through the flues *b'*. Opposite to the top hole *c* is a lateral working door, through which the metal is charged into the furnace.

In England the charge is 2½ to 4 tons of matte, whilst the larger American furnaces will take up to 8 tons. The metal is charged in England in pigs of about 3 cwt. each, so arranged that the air can circulate round each pig. No fluxes are added; the slag is derived partly from the sand adhering to the pigs which are cast in a sand-bed, partly from the quartz of the furnace bed.

The metal is heated slowly with free access of air until it softens, and is left for some time in this condition; it is then melted down very slowly drop by drop, whereby the sulphides of the matte are in part converted into oxides, which latter react upon the sulphides, both whilst the metal is in a pasty condition, and whilst it is being melted down, which takes from six to eight hours. The above reaction now

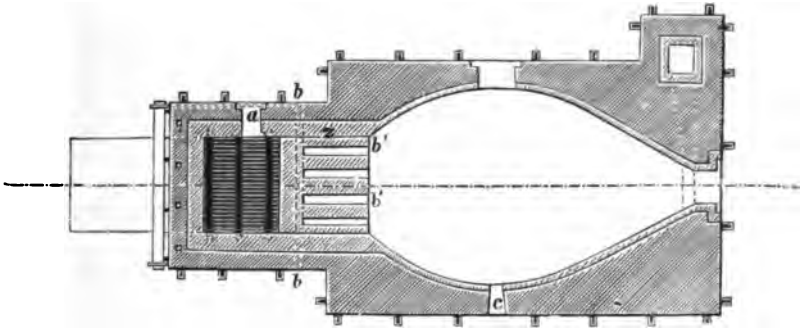


FIG. 106.

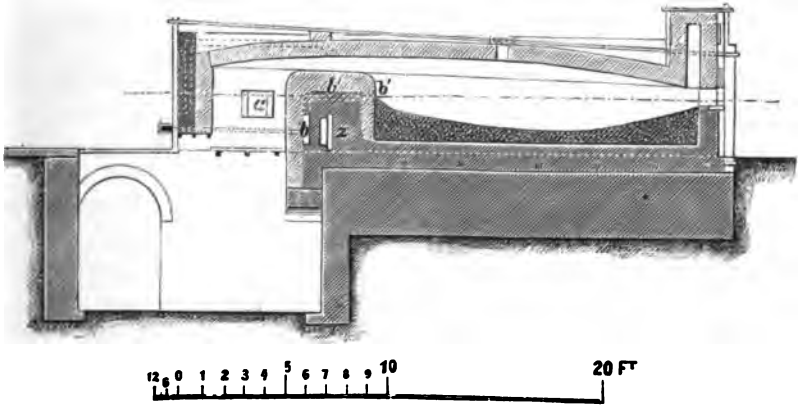


FIG. 107.

continues on the bed of the furnace, while bubbles of sulphur dioxide escape from the molten mass. As soon as the evolution of gas slackens, the slag that has been formed is skimmed off, and the temperature is lowered by opening the firedoor. The sulphur dioxide, which is still being formed, tries to break through the cooling surface of the molten mass, and covers it with protuberances and crater-like excrescences. The surface of the contents of the hearth is thus materially increased, and a larger area is exposed to the air for the

oxidation of the copper and the metallic sulphides, cuprous oxide being more especially produced. After a given time (four to five hours) the reaction of the oxides with the sulphides is again brought about by raising the temperature. The cuprous oxide is dissolved by the already formed metallic copper, and thus distributed through the entire mass, where it acts upon the sulphide of copper that is still present, forming copper and sulphur dioxide. After eighteen to twenty-four hours from the time of charging, the doors and the airchannel of the firebridge being all closed, a strong fire is put on so as to complete the reaction, to slag off any oxides that are present, and to separate the copper from the slag; the latter is then drawn off and the copper tapped into sand moulds.

With charges of 3 to 4 tons, the process takes twenty-four hours, with 8 ton charges about twice as long. The consumption of fuel is 60 per cent. of the weight of white metal.

On the average, English white metal yields 60 per cent. of coarse copper and 8·7 of rich slag, called *roaster* slag. The coarse copper is full of cavities, and is known as *blister* copper. Its composition is shown by the following analyses by Le Play:—

	I.	II.	III.
Cu	97·5	98·0	98·5
Fe	0·7	0·5	0·8
S	0·2	0·3	0·1
Sn and Sb	1·0	0·7	—
O and loss	0·6	0·5	0·6

Roaster slag is vesicular and contains 20 to 40 per cent. of copper; according to Le Play its composition is:—

Silica	47·5 per cent.
Ferrous oxide	28·0 „ „
Cuprous oxide	16·9 „ „
Alumina	3·0 „ „
Oxides of nickel, cobalt and mangane	0·9 „ „
Tin oxide	0·3 „ „
Metallic copper	2·0 „ „

It also often contains sulphide of iron.

This slag is added to the charge in the metal furnace.

THE ENGLISH PROCESS WITH REPEATED CONCENTRATION OPERATIONS

(*Welsh Process*)

This process is more particularly carried out in the neighbourhood of Swansea in South Wales.

The ores are first calcined and then, as explained above, smelted for coarse metal with 30 to 35 per cent. of copper. The subsequent treatment of this metal depends upon its purity, upon the quality of the copper which the smelter may wish to produce to meet the demands of the market, and upon the quantity and nature of the fluxes on hand in the form of either natural oxidised ores, such as carbonates of copper and cuprite, or of metallurgical products such as calcined mattes and slags containing copper. By regulating the quantity of oxidised additions as also the degree of calcination, it is possible to produce not only mattes richer in copper and lower in sulphur, but also a certain amount of coarse copper in the course of the smelting. As this coarse copper, so-called bottoms, takes up the tin, arsenic and antimony, that may have been present in the coarse metal, bottoms and purer mattes are produced, whenever it is required to prepare the purer qualities of copper from impure metal; the purer matte thus obtained is then treated further for the extraction of high grade copper, whilst the bottoms are worked up for inferior qualities (*tile copper*).

From pure coarse metal, concentrated mattes are produced that can be smelted direct for coarse copper; for impure metal on the contrary, the process of concentration, with the production of bottoms in the case of need, is repeated one or more times.

Matte concentration is performed either by calcining the coarse metal according to any one of the already described methods, followed by smelting in reverberatory furnaces with or without the addition of oxidised materials, or else by the above described roasting process; it is not carried quite as far as when blister copper is to be produced, the products being a concentrated matte and slag. This roasting process takes a good deal of time and is therefore but rarely employed except in the Welsh process proper.

The concentrated mattes are also smelted for blister copper by the same roasting process as already described.

The slags rich in copper produced in these concentrating operations are smelted with pyritic copper ores in reverberatory furnaces, and produce various grades of matte and certain quantities of coarse copper (bottoms). If the copper ores used contain tin, a tin-copper

alloy, known as *hard metal*, which is used in that form in the arts, is found to separate out between the bottoms and the matte.

The bottoms collect, besides tin, antimony and arsenic, the whole of the gold and a part of the silver of the matte, and are treated for gold whenever they contain this metal in workable proportions. The copper produced from them is of inferior quality.

The following are the various methods by which coarse metal may be worked:

1. (*a*) Calcination of coarse metal.
 (*b*) Smelting for white metal.
 (*c*) Roasting white metal for blister copper.

This method is employed when copper of ordinary quality is required. The calcined coarse metal is smelted with sufficient oxidised material to yield white metal with about 75 per cent. of copper. This is in fact the English process in its simplest form. If copper of better quality—so-called *tough* copper—is required, the amount of oxidised ores added is increased, so as to produce a certain proportion of bottoms.

2. (*a*) Calcination of coarse metal.
 (*b*) Smelting for *pimple metal*.
 (*c*) Roasting pimple metal for blister copper.

This method is employed when it is desired to obtain blister copper from pure coarse metal in a relatively short time. In this case the calcined coarse metal is smelted with more oxidised materials than when white metal is to be made. *Pimple* metal, as its name implies, is full of cavities and always contains metallic copper. Its percentage of copper is 78. If, owing to the addition of still larger quantities of oxidised materials, it is still richer in copper, or contains a larger quantity of metallic copper, it is called *close regulus*.

According to Napier, pimple metal contains on the average:—

Copper	78 per cent.
Sulphur	18 „ „
Iron	2 „ „
Slag	2 „ „

The slag, produced in this process contains according to Napier:—

Silica	60·4 per cent.
Ferrous oxide	36·1 „
Copper	3·5 „

3. (*a*) Calcination of coarse metal.
 (*b*) Smelting of the above for *blue metal*.
 (*c*) Roasting the blue metal for *special white metal*.
 (*d*) Roasting the special white metal for blister copper.

This process is applied when high qualities of copper (*best-selected* copper) are to be made. The *blue metal* which is first made, contains on an average 55 per cent. of copper; to produce it, the coarse metal is either calcined slightly or is smelted with but small additions of oxidised ores or metallurgical products. Blue metal has a bronze colour, but when broken hot, the fractured surface is blue; its composition is as follows, according to Le Play :—

Copper	56·7 per cent.
Iron	16·3 „
Nickel and a trace of manganese.	1·6 „
Tin and a trace of arsenic	1·2 „
Sulphur	23·0 „
Slag	0·5 „

Blue metal contains metallic copper, which is not the case with white metal. This copper occurs in fibrous, hair-like or wire-like forms, or in coherent powdery masses in the vesicular cavities of the metal, and is known as *moss copper*. Its composition, according to Le Play and Napier, is as follows :—

	Le Play.	Napier.	Napier.
Cu	98·2	98·5	99
Fe	0·4	trace	trace
Ni	0·6	—	—
S	—	0·4	0·4
Sn and Sb	—	1·0	0·5
Sand and carbon	trace	—	—

Moss copper is produced as explained in the case of *dünnstein* (*see* page 118). Hampe[1] has shown that molten cuprous sulphide is capable of dissolving copper at high temperatures and letting it separate out on cooling as moss copper if rapidly cooled, but as a reguline mass if cooled slowly. This explanation was given many years ago by Percy, who pointed out that when this metal, containing moss copper is re-melted, the molten mass is homogeneous and does not form two layers of copper and matte respectively.

The slag produced is the same as in smelting for white metal and is added to the charge in ore smelting and metal smelting.

At some works, the coarse metal is not calcined before being smelted, but is roasted direct for blue metal (as at the Cwm Avon works). In this case the coarse metal is charged in 3 cwt. pigs, heated

[1] *Chemiker Zeitung*, 1893, 17, No. 92.

for 4½ hours till it becomes pasty, and melted down during ¾ hour at a high temperature.

Blue metal is roasted in the way already described, the charge being 32 cwt. at a time; when the roasting is complete, the slag is skimmed and the metal run into sand moulds. Two charges are worked off in 24 hours.

The special white metal produced contains 77 per cent. of copper; the slags are rich in copper and are for the most part treated by the slag-smelting process to be presently described under (5).

The roasting of the special white metal is conducted in the ordinary way.

4. (*a*) Calcination of coarse metal.
 (*b*) Smelting for blue metal.
 (*c*) Roasting for special white metal.
 (*d*) Roasting the special white metal for *fine metal*.
 (*e*) Roasting the fine metal for blister copper.

This method is used for the preparation of the better grades of copper; it is conducted like the foregoing one, as far as the roasting for special white metal. This latter is roasted together with two other kinds of matte obtained by melting slags with copper pyrites, the so-called *red* and *white slag metal*. These two latter compose one-fifth of the total charge, which amounts to 30 cwt. The operation is a short one owing to the small amount of copper present; it takes 3¾ hours, of which 2¼ are occupied by the oxidation. In consequence of the large amount of cuprous oxide contained in the slag, a partial separation of the copper as bottoms occurs; 100 parts of charge produce 64 parts of fine metal with 81 per cent. of copper, 10 parts of bottoms with 92 to 93 per cent. of copper and 11 to 12 parts of slag with 11 per cent. of copper.

The fine metal is roasted for blister copper.

5. (*a*) Smelting cupriferous slags for red and white slag metal.
 (*b*) Roasting the red and white slag metal together with special white metal for fine metal.
 (*c*) Roasting the fine metal for blister copper.

The slags produced in the various smelting operations for white-metal, special white metal and fine metal are smelted with quartzose copper pyrites mixed with a little culm, the products being matte and bottoms. The matte is either very pure white metal or else, with charges rich in sulphur, red metal having a composition similar to blue metal. If the ores or the mattes contain tin, a white brittle alloy of copper and tin, known as *hard metal*, forms a layer above the bottoms. The charge is about 2 tons, and is worked off in five and

three quarter hours; the white metal contains 74 to 75 per cent. of copper, the red metal about 62 per cent.

The hard metal contains 66 per cent. of copper and 28 per cent. of tin, and is an article of commerce. The slags can be thrown away. The subsequent treatment of the red and white slag metal has already been described.

TREATMENT OF COPPER BOTTOMS

The copper bottoms produced in the various processes of matte concentration, contain the impurities of the mattes which would remain in them if bottoms were not made, especially arsenic, antimony, tin, nickel and cobalt. Bottoms, as already said, are produced with the object of obtaining pure mattes for the preparation of high grade copper. This pure matte is called *spongy regulus*.

The composition of bottoms is shown by the following analyses:—

	Napier.	Le Play.
Cu	74·6	86·5
Sn	13·8	3·2
Sb	4·5	0·7
Pb	0·8	1·8
Fe	2·5	6·9
S	3·9	—

The bottoms are either added in certain proportions to the various mattes when these latter are roasted for blister-copper, or they are roasted by themselves for blister-copper. The latter is refined and forms the lower grades of copper, known in commerce as cake copper when in the form of bars, or as tile copper when in the form of slabs.

Quite recently attempts have been made by Gilchrist, the inventor of the basic lining for the Bessemer converter, to use it also in roasting bottoms. The results of replacing the quartzose bed by a basic one appeared to be satisfactory, and induced an English works to have all its furnace beds thus altered. The basic bed is composed of calcined dolomite, which is stamped in layers into the reverberatory furnace and then fired; its advantages are that, when the bottoms are roasted on it, far less copper is slagged off than on a siliceous bed, and that with arsenical bottoms the bed is far more durable than a siliceous one. The oxidising roasting of bottoms for the purpose of freeing them from impurities, and especially from arsenic, takes a very long time, in consequence of which much copper is oxidised and the bed is strongly attacked. On a siliceous bed the copper is slagged off,

which occurs to a very small extent only on a basic bed according to Gilchrist's experiments; in the latter case, not only is less slag formed, but it is also poorer in copper. According to Gilchrist's experiments, when the same quantity of bottoms was treated on an acid and on a basic bed, only half the amount of slag was produced on the latter, and it contained only 25 per cent. of copper as against 55 per cent. on the former. Furthermore, when arsenical bottoms have to be treated the operation lasts so long that a quartzose bed becomes seriously damaged, and the lining has often to be renewed after a very short time, whilst with a basic bed these objections do not hold. Other metallurgists have, however, raised objections to basic beds, and these latter have not yet come into general use.

When the bottoms contain gold or silver, the precious metals are extracted by dry methods, wet methods, or electrolytically.

EXAMPLES OF THE ENGLISH PROCESS OF COPPER SMELTING

The English process, with all the above indicated modifications, is employed in the South Wales works, especially in the neighbourhood of Swansea, as also at St. Helens, near Liverpool. The largest English works are Vivian's Copper Works, near Swansea, known as the Hafod Works. In these English works, the objects of treatment are chiefly foreign ores and mattes from Chili, Cuba, Italy, Spain, Africa, and Australia. Since Chili has commenced to treat a large proportion of its own ores, the production of the English works has fallen off considerably. Besides Chili, the English process is used in Australia, North America, and Lapland. In Germany it was formerly in operation at the Elbkupferwerk, near Hamburg; at the Aggerthal Copper Works, near Duisburg, and at Dillenburg; and is still used at the Tubalkain Works, near Remagen, on the Rhine.

At the Chilian works at Guayacan, Panucillo, Carrisol and Lota, the ores are calcined and smelted for coarse metal with 50 per cent. of copper; this is then roasted for blister-copper, which contains 95 to 96 per cent. of copper, and is subsequently refined.

At the smelting works at Wallaroo, ores containing 18 per cent. of copper are calcined in continuous-acting rotating cylinders down to 5 per cent. of sulphur, mixed with lump ores calcined in stalls, low in sulphur, and smelted for coarse metal with 50 per cent. of copper, 12 tons being smelted in twenty-four hours. The coarse metal is in part calcined in rotating cylinders, then mixed with raw metal, and roasted for blister-copper, which is afterwards refined.

Gold and silver ores are also smelted there with copper ores pre-

viously calcined in rotating cylinders, in the already (p. 138) described large reverberatory furnaces, which treat 25 tons in twenty-four hours. The coarse metal thus obtained is partially calcined in rotating cylinders, and then smelted for bottoms and a rich matte. The bottoms were to be treated electrolytically (this process was not yet in operation when the author visited Wallaroo), whilst the rich matte was first to be desilverised by the Ziervogel process (*see* Silver, *supra*), and then treated for copper by reduction of the oxides and refining.

At the Argo works in Colorado, copper, silver and gold ores are treated. The ores are first calcined in an O'Harra furnace, and then smelted in large reverberatories with a daily capacity of 30 tons, producing argentiferous coarse metal with 40 per cent. of copper and 300 ounces of silver to the ton. This coarse metal is calcined in long-bedded reverberatory furnaces, and smelted for a second matte with 60 per cent. of copper. The latter is desilverised by the Ziervogel process, the residue from which, consisting essentially of oxide of copper with a small quantity of oxide of iron, partially freed from silver, is smelted with pyritic copper-bearing gold ores, producing bottoms and matte. This matte is also desilverised by the Ziervogel process. If it is then free from gold, it is reduced, and the copper obtained is refined; if it still retains notable quantities of gold and silver, it is sold to works, where it is treated with sulphuric acid for the production of bluestone, and the gold and silver extracted from the residues.

The bottoms are purified in the dry way, the gold concentrated in them and finally separated by a wet method.

The English process is also used in Montana; at Anaconda and Butte city, however, matte concentration has been displaced by the converter process.

At the Tubalkain works, near Remagen, in Rhenish Prussia, ores containing 8 to 10 per cent. of copper are smelted for coarse metal in 1 to 1½ ton charges. This is calcined in reverberatory furnaces and then smelted in 24 cwt. charges to fine metal with 80 per cent. of copper; the latter is roasted in 34 cwt. charges for blister copper.

THE ANGLO-GERMAN PROCESS OF COPPER SMELTING

The English and German processes are combined at many works, in that the ore smelting is conducted in shaft furnaces, whilst the matte is concentrated in reverberatories, and the smelting for coarse copper is performed in either form of furnace.

Thus in England, the English process has been modified at some works by using the shaft furnace for ore smelting, because it is the cheaper method and because it produces clean slags that can be thrown away.

In Germany and Austria on the other hand, the German process has been modified by using the reverberatory furnace for matte concentration and sometimes also for the production of coarse copper. This modification has been applied both to impure ores free from silver and to argentiferous ores. Concentration in reverberatory furnaces, because carbon is not employed as the reducing agent, produces purer mattes than do shaft furnaces, such mattes being required for the production of pure copper, as also for many of the methods of extracting silver; it is also much easier to collect any gold, that may be present in the ore, in the bottoms.

The combined Anglo-German process is in operation at Mansfeld, Oker, Brixlegg, and Bischofshofen (in the Salzburg district).

In the works of the Mansfeld Company the so-called *Kupferschiefer* (copper schist) is treated. It consists of bituminous schists with 1·8 to 3·7 per cent. of copper in the form of sulphuretted copper ores (bornite, chalcopyrite and chalcocite) and a small proportion of silver, equal to 0·53 to 0·63 per cent. of the copper present.

In addition to the above, *Kupferschiefer* contains, according to Berthier :—

Silica	40·0 per cent.
Alumina	10·7 „
Oxide of iron	5·0 „
Carbonate of lime	19·5 „
Carbonate of potash	2·0 „
Water and Bitumen	10·3 „

This ore is calcined in heaps to remove water and bitumen and is smelted in the already described (page 100) high shaft furnaces, yielding coarse metal with 30 to 40 per cent. of copper. This is calcined in kilns and smelted in reverberatory furnaces, forming a matte with 72 to 76 per cent. of copper, and on the average 0·45 to 0·48 per cent. of silver. This is treated by Ziervogel's process, and the residue, consisting of oxide of copper and a little oxide of iron is mixed with coal, reduced in reverberatory furnaces, and refined direct.

The heaps for burning the bitumen out of the schist have been previously described (page 38).

The charge for smelting in the modern Mansfeld furnaces,

described on page 100, consists of 17 cwt. of burnt schist, 6 cwt. of non-bituminous limestone known as *Dachberg*, which contains a small amount of silver and copper, 1 cwt. of slags containing copper, and 1 cwt. of skimmings, the conditions as to capacity, blast, &c., being those previously given. The furnace gases are used partly in heating the blast in iron stoves up to 200° C, and partly for raising steam. The matte contains 36 per cent. to 40 per cent. of copper, and 0·18 per cent. of silver; the slag contains 0·2 to 0·3 per cent. of copper. It is annealed, and then used as a building material. It is a mixture of bi- and tri-silicate, its composition being given on page 90. The furnace campaigns last from nine months to two years. In consequence of the use of heated blast and of the shape of the furnace, iron is reduced, which is tapped off from time to time through a hole in the bottom of the hearth; it contains nickel and is sold to nickel works. The flue dust contains about 14 per cent. of lead. It is mixed with ground shale, and pressed into bricks which are burnt with the schist and finally smelted in shaft furnaces, producing lead with 0·3 to 0·4 per cent. of silver. The coarse metal is calcined in kilns that put through about 1¼ tons in twenty hours, the gases evolved being led into lead chambers for sulphuric acid making at the Kupferkamme and Eckart works.

The calcined matte is smelted as described above, page 142, in reverberatories, the result being a matte of the following composition:—

Copper	70 —75	per cent.
Silver	0·4— 0·5	„
Iron	3 — 4	„
Lead	1·8— 2·1	„
Zinc	1·3— 3·3	„
Nickel and Cobalt	0·6— 0·9	„
Sulphur	20 —22	„

The slags contain 34·8 to 35·7 per cent. of silica and are added to the ore furnace charge on account of their containing copper.

By calcining the matte more strongly (by putting a part of it several times through the kilns), bottoms are produced in smelting. These contain all the gold of the matte, 0·93 per cent. of silver and 97 per cent. of copper and are treated electrolytically. The rich matte is desilverised by the Ziervogel method, reduced and refined.

At Oker the copper ores of the Rammelsberg, near Goslar, are treated; these consist of a mixture of copper pyrites, iron pyrites, zinc blende, galena, barytes and other gangue. They are separated

into four classes, Nos. I., II., III. and so-called *mixed ores*, which are distinguished by a relatively high proportion of lead (8 to 9 per cent.).

The average composition of the ores is shown in the following table :—

	No. I.	No. II.	No. III.	Mixed ore.
Ag	0·016	0·008	0·006	0·016
Cu	17·19	0·14	4·49	4·78
Pb	4·19	2·36	1·32	8·84
Zn	11·67	5·80	4·28	21·25
Fe	23·39	32·21	35·55	12·55
S	31·88	37·86	39·32	24·11
Residue	6·19	5·10	4·78	19·19

The ores contain 0·00005 to 0·0001 per cent. of gold.

The richer lump ores (No. 1. ores) are smelted raw, because they decrepitate in the heat and cannot be calcined in shaft furnaces, heaps or kilns. The other classes of ore are calcined in shaft furnaces, so that the gases evolved may be utilised in sulphuric acid making. Ores Nos. II. and III are calcined in pyrites burners and kilns down to 5 to 8 per cent. of sulphur. The mixed ores are calcined in kilns down to 10 to 12 per cent. of sulphur and then twice in heaps, till the sulphur is brought down to 5 to 6 per cent. All the concentrates are at present calcined in Hasenclever muffle furnaces down to 3 to 4 per cent. of sulphur, the gases evolved being used for the manufacture of sulphuric acid.

With the exception of the mixed ores which require special treatment on account of the quantity of lead they contain, the calcined ores are smelted in the five-tuyered shaft furnace described on p. 98, producing coarse metal with 30 to 40 per cent. of copper. This is calcined in kilns and smelted for rich matte containing 62 to 64 per cent. of copper and 0·06 per cent. of silver; the latter is calcined three times in heaps, and then smelted in reverberatory furnaces for black copper. The latter is in part refined and electrolysed, in part, after a partial refining, is dissolved in dilute sulphuric acid, producing bluestone and argentiferous residues, which are smelted with the addition of leady ores for argentiferous lead (work-lead).

The calcined mixed ores are smelted in the same kind of furnaces producing work lead, and a coarse metal called *bleistein* ("lead-matte") at Oker, containing 16 to 20 per cent. of copper, 4 to 5 per cent. of

lead, and 0·02 per cent. of silver. This lead-matte is calcined in kilns down to 7 per cent. of sulphur, and is then smelted in shaft furnaces, producing a matte with 30 to 40 per cent. of copper, and 0·06 of silver, and a leady speiss with 40 to 50 per cent. of copper, and 0·2 to 0·3 per cent. of silver. The former is treated in the same way as the matte produced in smelting the other copper ores, being in fact treated with it. The speiss undergoes scorification (*verblasen*) in a kind of reverberatory furnace, known as *spleiss* furnace, yielding work-lead, coarse copper with 97 per cent. of copper and scorification slags. The coarse copper is granulated and dissolved in dilute sulphuric acid, producing blue-stone and silver-bearing residues. The scorification slag is smelted in blast furnaces with raw copper ores, producing work lead, copper, matte and speiss, the matte being returned to the copper works.

The charge for smelting the copper ores is as follows :—

4 tons calcined copper ore Nos. I and II.
1 „ copper ore concentrates.
1¼ „ slags from the second matte furnace.
1¾ „ slags from the ore furnace.

With a blast pressure equal to 1·4 inches of mercury, 10 to 11 tons of ore are put through in 24 hours with a coke consumption of 28 to 30 per cent. of the weight of the ore.

A typical charge for smelting mixed ores is :—

3¼ tons calcined mixed ores.
1 „ concentrates.
¾ „ calcined pyritic ores.
¾ „ *Kniest* (clay slate containing chalcopyrite).
1¼ „ slag from the second matte furnace.
2¾ „ slag from the copper ore furnace.

With a blast pressure of 1·4 inches of mercury, 20 tons of charges, equal to 11¼ tons of ore, are put through in 24 hours, the consumption of coke being 33 per cent. of the weight of the ore, or 20 per cent. of that of the charge.

The lead-matte is calcined in the kilns described on p. 115, down to 6 to 7 per cent. of sulphur, and then smelted in furnaces of the old type with trapezoidal cross-section and 13 feet high, with 5 per cent. of *kniest* and 10 per cent. of ore furnace slag.

The matte (*bleistein-rohstein*) so produced is calcined in the kilns above mentioned with coarse metal, and matte obtained from the scorification slags, in the proportion of 50 parts of the first, 25 of the second, and 25 of the third; for every 100 parts of raw mattes, 20 to 30 parts of calcined mattes are added. In 12 hours, 3 tons of matte,

raw and calcined, are calcined down to 12 per cent. of sulphur. The calcined matte is smelted for concentrated matte in the reverberatory furnace described on page 142. The charge consists of 2½ tons calcined matte, ¼ ton raw matte and ¼ ton *kniest*, and is worked off in 8 hours with a consumption of 55 per cent. of coal. The slag contains 2 to 3 per cent. of copper, and is added to the charge in the ore smelting furnace. The matte produced is calcined three or four times in heaps down to 4 to 5 per cent. of sulphur, each heap containing 90 to 100 tons of matte, and requiring 353 cubic feet of wood; the first calcination lasts 3 weeks, each of the others a week to a fortnight.

The calcined matte is smelted in 4½ ton charges with the addition of copper refinery slag up to ½ ton, in a furnace like that used in the last operation, for black copper (*see* page 142). The operation lasts 12 hours, the consumption of coal being 55 to 57 per cent.

The black copper contains 92 to 95 per cent. of copper and 0·185 per cent. of silver; the slag from the first skimming contains 5 to 6 per cent. of copper, and from the second 20 to 25 per cent.; these are added to the ore furnace charges.

At Brixlegg, fahlores and argentiferous copper pyrites are calcined in heaps, and then smelted in shaft furnaces for coarse metal; the latter is calcined in heaps and then smelted in reverberatory furnaces for concentrated matte, which is crushed, calcined in long bedded reverberatory furnaces and smelted in circular shaft furnaces for black copper.

At Bischofshofen, arsenical copper pyrites free from silver, containing 12·5 per cent. of copper is smelted raw in circular shaft furnaces for coarse metal with 21 per cent. of copper. The latter is calcined in heaps and smelted in circular shaft furnaces for concentrated matte with 53 per cent. of copper. This latter is calcined twice in heaps, and is then smelted in reverberatory furnaces for fine metal with 76 to 78 per cent. of copper. This is one half calcined in long bedded calciners, and smelted with the other half raw in reverberatory furnaces for coarse copper. The coarse copper is refined in reverberatory furnaces.

Copper Extraction by means of the Converter, or the Copper Bessemer Process

The copper Bessemer process is not an independent process, but has for its object the production of coarse copper from mattes which have been obtained from ores by the German, the English or the

Anglo-German process. Raw ores are not suitable for the converter process, because, in consequence of their high percentage of iron and of the admixture of earthy and siliceous matter, they would produce more slag than could be kept liquid by the heat developed by the oxidation of the metallic sulphides in the converter; moreover they would attack the lining of the converter too vigorously.

The copper Bessemer or blowing-process, is as above noted, a shortened English process for obtaining copper from matte. Its principle is that a blast of air forced through molten matte will convert the sulphides of iron and copper into ferrous and cuprous oxides with the evolution of sulphur dioxide. The cuprous oxide decomposes the sulphide of copper that has not yet been oxidised with the production of copper and sulphur dioxide, whilst the ferrous oxide is slagged off by the silica of the converter lining. The heat developed by the oxidation of these sulphides, especially by the formation of sulphur dioxide and ferrous oxide, suffices to keep the mass fluid during the process. If the blast is continued long enough, coarse copper and slag are obtained; if the process is interrupted earlier, a matte rich in copper and slag result. Matte containing but little copper will not yield coarse copper direct, because too great a quantity of slag would form, which could not be kept fluid. In this case the operation is stopped as soon as a certain quantity of slag has been formed, when a rich matte is produced which can be brought up to coarse copper by means of a second converter operation. As the production of matte rich in copper from poor matte, attacks the expensive quartz lining of the converter very violently, whilst a proportionately large quantity of copper goes into the slag, it is in most cases found preferable to produce a matte with at least 25 per cent. of copper by the German, English, or Anglo-German process, and to bring this up to coarse copper at one operation in the converter. Poor matte is blown up to 60 to 70 per cent., when the slag is removed, a fresh quantity of matte added and coarse copper with 99 per cent. of copper is blown.

The matte to be bessemerised is either melted in cupolas and then run into the converters through gutters of iron lined with a mixture of quartz and clay, or it is tapped direct from the shaft furnaces in which it is produced, as at Röros.

The apparatus in which the operation is performed may be constructed like the Bessemer converter, or may be cylinders capable of revolving, or of a type intermediate between the two.

These of the first type differ from regular Bessemer converters in their small capacity, holding from 1 to 3 tons of matte as against

10 tons of pig iron in the Bessemer converter, and in the position of their tuyeres. In the ordinary Bessemer converter these are situated in the bottom, in the copper converter round the sides at a certain distance above the bottom. When pig iron is converted into ingot iron, the mass in the converter is always homogeneous and is developing heat uniformly throughout by the oxidation of its silicon, carbon and iron, and in some cases of phosphorus; there is, therefore, no danger of one part of it solidifying. When matte, however, is blown in the converter, the heat is produced by the oxidation of the sulphides, whilst the metallic copper, produced as already explained, collects on the bottom of the converter. If the blast entered at the bottom it would therefore be necessary for it to pass through the

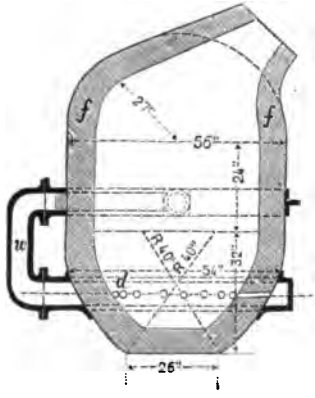


FIG. 108.

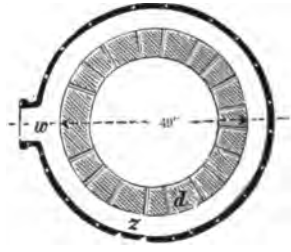


FIG. 109.

fluid copper before it could reach the fluid matte and in doing so it would partly oxidise the copper to cuprous oxide. So little heat would, however, be thereby generated, that the copper would soon chill and the process come to a standstill. This is the reason why the earlier attempts at blowing matte in the converter were failures for so long a time. Manhés was the first to succeed in making the process applicable to matte by placing his tuyeres in the sides above the highest level that would be reached by the copper produced.

The arrangement of the Manhés converter at Eguilles near Sargues in Vaucluse, is shown by the subjoined Figs. 108 and 109. The converter is 6 feet 6 inches in height and 4 feet 7 inches in diameter in the widest part. The tuyeres *d* are 6 inches above the bottom and are 0·5 to 0·6 inches in diameter, there being at least 20 of them. They are made by piercing the lining which consists of a mixture of quartz with enough clay to make it plastic, before it has

dried, with a pointed iron rod. All the tuyeres lie in one plane and converge to the centre. The lining *f* is 12 inches thick on the bottom, 10 inches in the lower part of the walls and only 6 inches in the upper part of the converter. The blast pipe *w* is attached to the converter and revolves with it ; *z* is the blast main surrounding the converter, from which the blast escapes through the tuyeres into the molten mass inside the converter. Opposite each tuyere there is an opening in the blast main which is kept closed by an iron plug; these can be removed when the tuyeres need pricking out. The

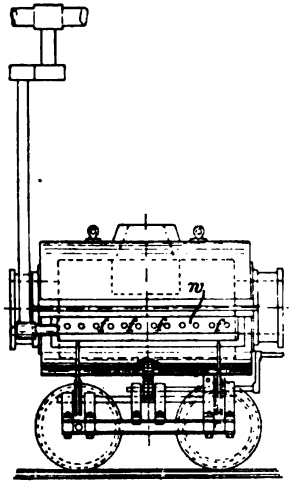


FIG. 110.

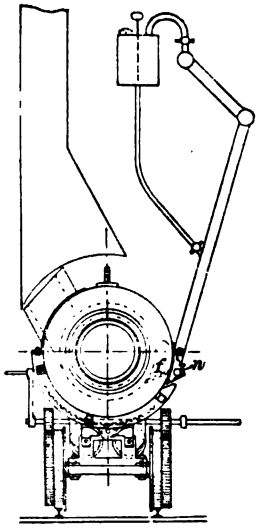


FIG. 111.

blast pressure in converters of this class is equal to 12 to 20 inches of mercury.

Cylindrical converters have been constructed by Manhés and David. In these, mattes with a moderate proportion of copper (26 per cent.) can be blown direct to coarse copper, though of course the output is comparatively small.

The construction of such a converter is shown in Figs. 110 and 111. The tuyeres are situated at one side of the cylinder; the blast chest *w* can be rotated with the cylinder. By turning the cylinder suitably it is possible to send the blast into the molten bath in such a way that no portion of the matte escapes oxidation. When the Bessemer converter is used on poor mattes, a concentrated matte collects on the converter bottom, which on account of its small

volume does not rise above the level of the tuyeres and thus escapes oxidation; in such cases therefore rich matte would be produced instead of coarse copper. This difficulty is overcome by the use of the above mentioned cylinders, as by rotating the cylinder the blast can be turned in any desired direction. The blast pressure in these converters is 10 to 15 inches of mercury.

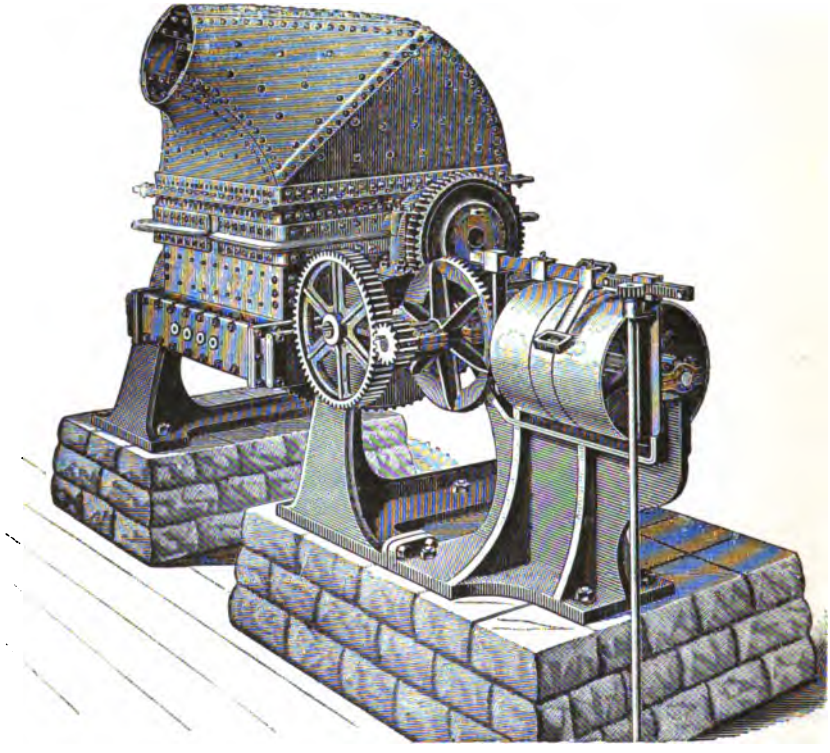


FIG. 112.

Recently James Douglas has erected a converter of this pattern at the works of the Copper Queen Company at Bisbee, Arizona.

Converters intermediate between the Bessemer converter and the cylindrical pattern, the so-called Stalmann converter, were in use till quite recently at the Anaconda works in Montana and at the Nicholson chemical works at Brooklyn. Fig. 112 shows the external appearance of this form of converter; it has three flat sides an arched side and a concave bottom. The blast chest surrounds the flat front and the two flat sides; by this arrangement the blast may be injected into any part of the converter, whilst by suitably turning

the latter, the depth of the layer of molten material over the tuyeres can be increased or diminished. Only the tuyeres in the front are used in regular work; those at the sides are used when the lining of the converter has been eaten away by the boiling up of the molten mass. When this happens, the contents is not run out as would have to be done with the other forms of converter, but the blast is cut off from the side opposite to the corroded portion. This stops the ebullition at that point and the operation can be continued till the blow is finished and then the defective spot can be repaired. When the blast is stopped at one side, the tuyeres on the other sides must supply the air required. The back side of the converter is so bent as to correspond to the curve of ebullition, whereby the injury to the lining of that side by the boiling up of the molten mass is reduced to a minimum.

The projection of molten mattes from the throat of the converter is largely prevented by its shape, as anything spurting up must strike against the upper wall of the converter and for the most part drop back again into it.

To facilitate the relining of the converter, the upper half is bolted to the lower. If it is not to be taken apart, it must be cooled by pouring water into it, and, after it has been lined, be dried by a wood and coke fire. The lining is best made of crystalline quartz, crushed down to pea size and mixed with only enough clay to hold it together. For continuous working, a plant of 3 such converters is required, one being in operation whilst another is being cooled or lined, and the third is being heated up. The quantity of copper that can be produced in such a 3-converter plant in 24 hours is:—

15 tons with matte containing 60 per cent. of copper.
12 „ „ „ 50 „ „
8 „ „ „ 40 „ „

When the lining, 16 inches in thickness, is new, the charge amounts to 1½ tons which is gradually increased to 4 tons as the lining gets eaten away. The blast pressure is equal to 16 inches of mercury.

The matte is remelted in a cupola furnace and is run into the converter, which is turned down into a horizontal position, through an iron gutter lined with a mixture of quartz and clay.

Matte of 60 per cent. is blown direct to coarse copper. With poorer matte, containing from 30 per cent. of copper upwards, the blast is stopped after 20 to 25 minutes; the slag is then poured out into slag pots set below the converter, and the blow is continued till it is finished. The charge has been converted into copper when

the evolution of sulphur dioxide ceases, and little particles of copper appear in the flame.

At Anaconda the blast is furnished by a tandem blowing engine; the steam cylinder is 18 inches in diameter, the blowing cylinder 40 inches; the stroke is 3 feet 6 inches.

At the Parrot works and the Anaconda works, in Montana, where the author has seen the converter process in operation, a converter will stand about 12 charges before it needs relining.

The matte is generally remelted in cylindrical shaft or cupola furnaces. At the Parrot works 50 tons of matte are melted in 24 hours with the consumption of 8 per cent. of coke. At the Anaconda works waterjackets 3 feet in diameter at the tuyeres are used, the fuel consumption being the same.

The liquid matte is run into the converter, and the blast is at once turned on. At both the above works the charge is at first 1½ tons (3,000 lbs.),[1] which is increased as the lining is worn away to 2 tons at the Parrot, and to 4 tons at the Anaconda works.

Immediately the blast is turned on, a yellow flame appears together with white fumes of sulphur dioxide and trioxide. After 20 minutes the converter is turned down and the slag run off; it is then turned upright again and the blow continued till coarse copper is produced; this is run from the converter into iron moulds placed on a car. The process lasts from 45 minutes to 1½ hours, according to the size of the charge.

The copper is comparatively pure and is, *e.g.* at the Anaconda works, electrolysed direct; it contains 99 per cent. of copper and small quantities of iron and sulphur. Arsenic and antimony are completely volatilised; zinc is partly volatilised, partly slagged off; lead, tin and cobalt pass into the slag; nickel and bismuth remain in the copper.

The slag contains 2 to 5 per cent. of copper and is added to the ore furnace charge. A sample analysed for the Russian Ministry of Finance gave the following result:

Silica	35·70
Alumina	1·76
Ferrous oxide	55·83
Manganous oxide	0·22
Zinc oxide	0·86
Copper	2·14
Sulphur	1·03

[1] In America the short ton of 2,000 lbs. is used for most of the materials and products of copper works. It is equal to 0·9072 of the metric ton and 0·8929 of the English statute ton.

When poor matte is to be concentrated, the operation is stopped sooner. Thus at Eguilles, matte with 30 per cent. of copper is blown up to matte with over 70 per cent. in 30 minutes; the latter is remelted and blown to coarse copper.

The concentration of matte in the converter is but rarely attempted; it is more profitable to blow matte, concentrated in shaft or in reverberatory furnaces, direct to coarse copper.

At the Parrot works, matte with 50 to 60 per cent. of copper is blown up to coarse copper with 98 per cent. of copper and 100 ounces of silver to the ton. The converter, which is similar to that first described above, has a lining 3 inches to 4 inches thick; with a new lining the charge is one ton, later on 2 tons. The blast is furnished by a blowing engine of 200 horse power; when two converters are worked together 150 horse power are required. The blast pressure is equal to 14 to 20 inches of mercury. With three converters, 50 tons or 100,000 lbs. of matte are treated in 24 hours, and 25 tons or 50,000 lbs. of coarse copper are produced from it. The operation lasts 1½ hours on the average.

In the 24 hours, 4 men are required at the remelting cupolas, 3 for repairing converters, and 6 for working the converters.

At Anaconda, the above described Stalmann converters have been used; there are four blowing engines for four sets of 3 converters each. A converter requires 90 horse power; the blast pressure is 6 to 8 lbs. on the square inch, equal to 12 to 16 inches of mercury. The charge is at first 3,000 lbs. and afterwards 6,000 lbs. The matte contains 60 per cent. of copper and is blown up to coarse copper with 99 per cent. of copper and 99 ounces of silver to the ton in from ¾ hour to 1½ hours, according to the weight of the charge. After 20 minutes the slag is run off, and the blow continued till the operation is complete. The converter slag contains 2½ to 3 per cent. of copper.

At the works of Jeres Lanteira, Province of Granada, Spain, cylindrical shaped converters are being used.[1] Their diameter is 21½ inches; they are made of sheet iron and lined with a mixture of 75 per cent. of quartz and 25 per cent. of clay, which does not last above 24 hours. For continuous working 3 converters are required. The charge is 20 to 24 cwt. of matte with only 26 per cent. of copper. The blow lasts 40 minutes, and with the three converters 5 to 6 tons of matte are treated in 24 hours. The blast pressure at the commencement of the blow is equal to 10 inches of mercury, but rises at the end to 12 inches. Part of the slag has to be run off during the

[1] Terraillon, *Bulletin de la Société de l'Industrie minérale, St. Etienne*, tome v. 1891, p. 910.

operation. With the comparatively low amount of copper and high amount of iron in the matte, a great deal of slag rich in copper is produced, so that the direct production of copper is relatively low, being only 50 per cent. The resulting copper is said to contain only 0·5 per cent. of impurity.

At Röros in Norway, the same form of converter is used. The ores containing 5 per cent. of copper and 35 per cent. of sulphur are calcined in heaps down to 3·5 per cent. of sulphur, and are smelted in waterjackets producing a matte with 30 per cent. of copper. This is tapped direct into the converters, which hold from 16 cwt. to 1 ton of matte. The latter is blown with a blast pressure of ½ atmosphere (7½ lbs. on the square inch) in one hour up to coarse copper with 99·20 per cent. of copper, slag being run off two or three times during the operation. The coarse copper is refined in English reverberatory furnaces. The converter lining, made of a mixture of sand and clay, stands for 8 charges. Water supplies the motive power required.

Besides the above named places, the converter process is also used at Vivian's works in Swansea, at the works of the firm of Cousino at Lota (Chili), at those of the Société Metallurgique Italienne at Leghorn, at Bratsberg in Norway, and at the Nicholson Chemical Works in Brooklyn. Plants are in process of construction at a great many other works.

Pyritic Smelting

Considerable progress is being made with this novel process, particularly in the United States, the object being to produce matte suitable for the Bessemer process direct from the raw ore, the sulphur and iron of which are made to act as fuel. The furnaces used are either of brick or water jacketed. Pyritic ores, with if necessary fluxes and usually a small amount of coke are charged, and the blast used is strongly heated by independent firing. With hot blast the consumption of coke in the furnace has come down to 1½ per cent. of the weight of the ore, whilst 100 tons per day has been put through one furnace at Kokomo, Colorado.[1] It has not been found economically possible hitherto to dispense altogether with the use of carbonaceous fuel, a small amount, as indicated, being generally charged with the ore. It is stated that cold blast can under some circumstances be successfully used, but it would seem that the use of hot blast leads to notable economy of fuel consumption. It has been

[1] Peters, *op. cit.*, p. 437.

proposed to heat the blast by the waste heat of the furnace slags.[1] The feasibility of pyritic smelting has been quite established, but the process has hardly yet passed into regular use.

THE EXTRACTION OF COPPER FROM OXIDES AND SALTS OF COPPER, AND FROM ORES THAT CONTAIN NATIVE COPPER

Oxidised and acid copper ores, poor in copper, are either added to the furnace charge in smelting sulphuretted ores or mattes, or else, when they occur in considerable quantity, are treated by wet methods. Richer ores may be smelted with sulphuretted ores or mattes in the English process, or may be smelted alone with the addition of slags and other suitable fluxes for coarse copper. In the latter case, shaft furnaces are used; if reverberatory furnaces be used, carbon must be mixed with the ores for a reducing agent.

Ores that contain native copper only require their earthy gangue to be slagged off; this is best performed in reverberatory furnaces, and should be immediately followed by refining. The slags rich in copper thus produced are smelted in shaft furnaces for coarse copper.

The smelting of oxidised and acid copper ores was formerly carried on at Chessy near Lyons, and is now carried on, on a large scale, in the Urals and in Arizona and New Mexico.

At Chessy, in the years 1828 and 1829, carbonates and oxides of copper in a gangue of quartz and clay, containing 27 per cent. of copper, were smelted in shaft furnaces 6 feet high, with 20 per cent. of lime, 5 to 6 per cent refinery slags and 60 per cent. of slags from the same operation. In 24 hours 2½ tons of ore were treated with a consumption of 77 per cent. of coke. In the most favourable cases the slag still contained ½ per cent. of copper.[2]

At Perm in the Western Ural, sandstones containing 3 per cent. of copper as malachite, azurite, silicate, chalcocite and native copper, are smelted with the addition of dolomite and of slags from the same operation in shaft furnaces about 20 feet in height with fixed forehearths and elliptical in cross section, charcoal being used as fuel; the products are coarse matte, coarse copper and cupriferous pig-iron. The composition of these two latter products is as follows:—

	Coarse Copper.	Pig-Iron.
Copper	90·5	12·6
Iron	6·1	75·9
Vanadium	1·2	2·0
Silicon		2·5

[1] Herbert Lang, *Matte Smelting*. 1896, p. 67.
[2] Knab, *Métallurgie*, Paris, 1891, p. 122.

The cupriferous pig-iron is scorified with the addition of sand on a hearth with a highly inclined tuyere, with charcoal as fuel; the iron is thus oxidised and slagged off, whilst the copper is obtained as coarse copper.

In the States of Arizona and New Mexico, carbonates and oxides of copper are smelted in the previously described water-jacket furnace.[1] The various classes of ore contain so much silica, oxide of iron, and lime, that they need only be mixed in proper proportions to produce fusible slags, the addition of fluxes being rarely necessary. The carbonates of Arizona contain sufficient sulphur to prevent the copper from being slagged off, and to produce matte with 60 to 65 per cent. of copper. The furnace is of the crucible type, the bottom of the crucible being from 1 foot 4 inches to 2 feet below the tuyere level; if made deeper than this, there is danger of the copper chilling. The height of the furnace above the tuyeres does not exceed 7 feet. The furnaces are circular or rectangular in horizontal section. Circular furnaces are either cylindrical or else taper from the throat to the tuyeres. Rectangular furnaces are built like the already described Henrich furnace with boshes; the effect of these is said to be to increase the reducing action of the furnace gases and to yield cleaner slags.

The fuel used is coke with 11·6 to 14·6 per cent. of ash. The blast is produced by Baker blowers and has a pressure of 10 to 12 oz. on the square inch. The diameter of the tuyeres is usually 3 inches, exceptionally, as at the Copper Queen, 5 inches. The slag notches, which are often cooled by water, are 10 inches below the tuyeres and are continued as cast-iron gutters. The tap hole for the copper is in the lower part of the crucible. The slags are not allowed to run continuously, but are tapped off every 6 minutes into slag pots set in front of the furnace. The coarse copper is tapped periodically and run into moulds arranged on a carriage.

Each furnace will put through 70 tons in 24 hours. The coarse copper produced contains 97 to 98 per cent. of copper, the slag contains on the average 1·75 per cent.

The Copper Queen furnace is circular, 3 feet in diameter, has six tuyeres 5 inches in diameter, and smelts daily 40 to 50 tons of ore without fluxes; the similar furnace at the Old Globe Mine (Arizona) puts through 55 tons in the same time.

The table on following page from Peters' already quoted work shows the working conditions that obtain in the more important works of Arizona that are treating oxidised ores:—

[1] Peters, *op. cit.*

Name of the works.	Area of furnace at the tuyeres.	Number of tuyeres.	Total area of tuyere openings.	Blast pressure per sq. in.	Parts by weight of ore to 1 part coke.	Ore smelted in 24 hours.
	Sq. ft.		Sq. in.	Oz.		Tons.
Copper Queen	7	6	75	10	5·90	47
Detroit Copper Co., large furnace	11·8	14	83	12	6·55	79·15
,, ,, ,, small ,,	7	6	58	10	5·55	45
Arizona Copper Co., large ,,	12·5	6	64	10	—	—
,, ,, ,, small ,,	7	6	58	10	—	—
United Verde	7	6	58	10	—	52

The composition of the slags from the Copper Queen, Arizona is as follows :—

Silica	26·64
Ferrous oxide	42·60
Manganous oxide	0·30
Zinc oxide	0·50
Lime	9·51
Magnesia	0·20
Alumina	15·40
Alkalies, loss, etc.	4·85

The copper contents average 1·75 per cent.

The slag produced in a Henrich furnace at Clifton, Arizona, has the following composition according to S. James, Junr. :—

Silica	34·34
Ferrous oxide	32·27
Manganous oxide	6·24
Lime	10·13
Magnesia	2·30
Alumina	11·80
Alkalies, loss, &c.	3·64

The smelting of ores containing native copper is carried on at Lake Superior, in Detroit and in Pittsburg. It is performed in reverberatory refining furnaces and consists in simple fusion of the ores; the slag is then removed and the copper refined. The slags are smelted with refinery dross in shaft furnaces for coarse copper. This process is detailed under the head of refining.

2. PURIFICATION OF COARSE COPPER (IN THE DRY WAY)

Coarse copper obtained in the dry way still contains a number of foreign bodies that render it unfit for use in the arts, and which have

accordingly to be removed from it. These are principally: iron, lead, zinc, cobalt, nickel, bismuth, arsenic, antimony and sulphur. The separation of these elements from copper can either be brought about by the oxidising fusion of the coarse copper, or else by means of the electric current, copper purified to a certain degree in the dry way forming the anode.

By the oxidising fusion of coarse copper, its foreign constituents (with the exception of the precious metals) can be oxidised, because their affinity for oxygen is greater than that of copper, and either volatilised or slagged off; volatile substances can be volatilised direct.

If the coarse copper be used as the anode of an electric current, a solution of sulphate of copper acidulated with sulphuric acid being used as the electrolyte, copper in a pure state can be electrolytically transferred to a cathode consisting of sheet copper, whilst the various impurities either pass into solution, remain at the anode, or are precipitated. This method is, however, only practised when the copper is to be separated from gold, silver or nickel, because it would be too costly as a simple process of purification, unless the precious metals or an alloy with nickel were obtained simultaneously. Further details will be found under the head of the Electrolytic extraction of copper.

The principal method used for purifying copper, that contains no precious metals, is by an oxidising fusion.

By this operation a portion of the copper is always converted into cuprous oxide, which possesses the property of melting with copper to a homogeneous mass. A considerable proportion of cuprous oxide, however, diminishes the softness and tenacity of copper, as already stated. After the oxidising operation is finished, it is therefore necessary to reconvert the cuprous oxide into metal by a process of reduction.

Coarse copper is accordingly purified either by producing in one furnace copper containing cuprous oxide, which is then freed from cuprous oxide in a second furnace, or else the oxidation of the foreign elements and the reduction of the cuprous oxide produced, are performed directly afterwards in one and the same furnace.

The production of copper containing cuprous oxide in a special furnace is known as *gaarmachen* (nearly equivalent to "*refining*" in the English method), and the copper is called *Gaar Kupfer* (nearly equivalent to "*dry*" copper). The conversion of *Gaar Kupfer* into copper free from oxide in a special furnace is called *hammergaarmachen* (which may be rendered "*toughening*") and the copper is

called *hammergaares Kupfer* ("*tough pitch copper*" or "*tough cake*"). The conversion of coarse copper into tough pitch copper in one and the same furnace, without any interruption, is called *combined gaarmachen and hammergaarmachen* when the operation is performed upon a hearth, and the copper is called *hammergaares Kupfer*; when the operation is conducted in a reverberatory furnace it is called "*refining*" (this is the proper signification of the word in the English process), and the product is refined copper or *Raffinad.*

We may therefore distinguish :—

(1) The purification of copper by refining and toughening as separate processes.

(2) The purification of copper by combined refining and toughening in the hearth.

(3) Refining of copper in the reverberatory furnace (English method).

The two first methods, which were formerly extensively used in Germany, Sweden, Norway and Russia, are now only employed exceptionally, as they can only be conducted upon small quantities of metal, and necessitate a large expenditure on fuel and wages The third method of purification, which originated in England, is now universally employed, and should always be preferred as by far the most advantageous.

1. *Purification of copper by separate refining and toughening*

This method embraces the two processes of producing the dry copper (*Gaar Kupfer*) and the toughening of the latter.

(*a*) *The production of Gaar Kupfer* is carried out either in hearths or in reverberatory furnaces. Hearths are used when small quantities of the purer kinds of coarse copper are to be treated, whilst reverberatory furnaces must be employed on account of the stronger degree of oxidation needed, when larger quantities of impure coarse copper have to be dealt with. The hearth used is the so-called small refining hearth (*Gaarheerd* or *Kupfergaarheerd*). The reverberatory furnaces are generally worked with a blast, so-called *Spleiss* furnaces, or more rarely by draught.

Refining in the small refining hearth is a process requiring much fuel and admitting of only a small output, and hence is only exceptionally used in civilised countries (where, in consequence of old customs, pure dry copper is in demand for brass-making).

The refining hearth (Fig. 113) is an approximately hemispherical cavity, cut out in a mixture composed of one part by volume of

charcoal dust and seven to eight parts of clay, or a mixture of this with sand, or again, simply in clay; above it a hood for taking off the fumes is suspended. According to its size, a hearth will take from 3 cwt. to 30 cwt. of coarse copper; a medium-sized hearth is 2 feet in diameter and 1 foot deep. In the backwall *w* there is a tuyere *n*, which projects 1½ to 1¾ inches over the edge of the hearth, and is inclined at a steep angle, as much at times as 45 degrees, so that the blast may strike upon the fluid copper in the hearth. At the front side of the hearth there is a cast-iron working plate. In rare cases there is in front of the hearth a well, the so-called *reiss-heerd*, cut in a block of wood independent of the hearth, into which the refined copper is ladled, to be taken off from it in discs.

The coarse copper is either melted in small shaft furnaces, or else in the hearth itself upon a layer of fuel (charcoal or coke). In the latter case it is charged a little at a time in to the hearth, and is so disposed that only the edges and not the surfaces of the discs of coarse copper are turned towards the blast. The molten copper is kept covered with charcoal or light coke; as soon as a certain quantity of slag has accumulated, the fuel is cleared away and the slag skimmed off. The fuel is then replaced and removed before the next slag skimming, and the operation is thus continued until the copper is refined (*gaar*).

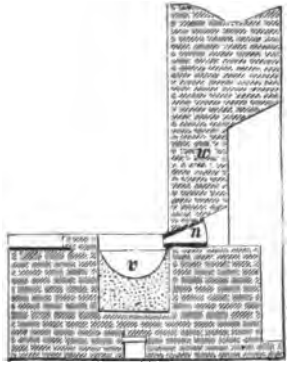


FIG. 113.

The action of the blast upon the melting coarse copper and upon the liquid bath of metal oxidises the foreign elements present and a portion of the copper itself. The cuprous oxide thus produced has also an oxidising action upon the foreign substances, in that it melts with the metallic copper and is diffused through the molten copper, where it parts with its oxygen to the foreign elements, and is thereby reduced to metallic copper again.

As the metallic bath is kept covered with carbonaceous fuel, it is inevitable that the latter should to some extent exert a reducing action on the oxides formed, and thereby prolong the operation. On account of the high temperature of the bath of metal, a part of the readily volatile metals present is volatilised without previous oxidation.

Of the various foreign elements, antimony, arsenic, zinc and lead are in part volatilised and in part oxidised, the non-volatile oxides

passing into the slag. Sulphur is volatilised as sulphur dioxide, being for the most part oxidised by the cuprous oxide. The non-volatile oxides, and especially ferrous oxide, form slag with the siliceous matter of the hearth. This slag is limpid when large quantities of oxide of lead are present, but pasty in the presence of large quantities of iron and nickel. At the commencement of the operation the colour of the slag is brownish black, on account of the predominance of iron in it; later on, as the proportion of cuprous oxide increases, it changes to red. Iron, zinc and lead are easily removed from coarse copper, but nickel, cobalt, bismuth, arsenic, antimony and the last portions of sulphur only with much greater difficulty.

Nickel passes in part into the slag, in part it remains with the copper, and is concentrated in the upper discs of the refined copper. If antimony is present as well as nickel, a peculiar substance forms in small glistening golden scales mixed with the copper, known as "*copper mica*"; its composition according to Hampe is $6Cu_2OSb_2O_5 + 8NiOSb_2O_5$.

Arsenic and antimony possess the property of delaying the oxidation of foreign bodies by rising up from the bath in the form of thick fumes, and thus impairing the efficiency of the blast.

In this operation there is always more cuprous oxide formed than is needed for the oxidation of the foreign elements. Under normal circumstances the copper produced will contain 6 to 8 per cent. of cuprous oxide. If, however, the coarse copper contained considerable quantities of arsenic, antimony and nickel, the length of time required in order to remove these bodies causes the formation of much greater quantities of cuprous oxide, up to 50 per cent. Copper with more than 8 per cent of cuprous oxide is called *übergaar*—("over refined" or too dry). This copper is brought back to its normal state by adding a small amount of lead or of coarse copper to the bath of metal, or by inserting into it poles of green wood; the gases evolved from the latter reduce the cuprous oxide to metal. Lead likewise has a reducing action on cuprous oxide, oxide of lead being formed; it is also capable of dissolving the above mentioned copper mica, and, in the form of oxide, it has an oxidising influence on other impurities such as nickel, arsenic and antimony.

Shortly before the completion of the refining, the so-called *spriihen* ("copper rain") takes place; this consists in the projection of a shower of little globules of copper from the molten bath. This phenomenon is due to the evolution of large quantities of sulphur dioxide from the bath of metal, in consequence of the reaction of

cuprous oxide on sulphide of copper when the bath has cooled down to a certain point.

The approaching completion of the operation is indicated by the red colour of the slag, the sea-green colour of the molten metal, the cessation of the evolution of the fumes, and the boiling up of the bath. The best indication is the character of a small sample called the *gaarspahn* taken from the bath. It is taken by dipping an iron rod with a conical point into the bath through the tuyere, and at once withdrawing it, the film of copper adhering to the rod forming the sample in question. If the refining is complete, this sample forms a thin netlike coating on the iron, wrinkled and crystalline on the outer surface; it is easily loosened by dipping the rod into water, is pliable, its inner surface shows a copper red colour and metallic lustre, and its fracture is close and of a cherry red colour. If the copper is not yet refined, in which state the Germans speak of it as *too young*, the sample is difficultly detachable, thick, outwardly smooth, inwardly of a yellow colour and very brittle. If it is over refined, the sample is thick, very brittle, and shows a dull reddish brown colour on its exterior surface.

After the refining is finished, the blast is stopped, the copper allowed to cool under a layer of coal dust and ladled into moulds or taken off in discs. In many cases the copper is ladled into a separate basin or hearth before it is made into discs (the so called "*rosette*" copper). This "*rosetting*" or disc-making requires a definite, not too high, temperature; when this has been attained, water is sprinkled on the surface of the copper, whereby a disc, detached from the sides of the hearth, and convex upwards, is formed. This disc is lifted off with a fork and thrown into water, when a second disc is at once made in the same way and lifted off, and so on.

According to the size of the hearth, from 80 to 100 discs or rosettes can usually be taken off; the first few are generally impure and over-refined, and are therefore added to the next charge to be refined.

The nickel, with the exception of what has passed into the refinery dross, usually accumulates in the topmost disc, in which, when antimony is present as well, the copper mica is also found to collect.

The time of the operation depends on the size of the hearth and of the charge, and varies between $1\frac{1}{2}$ and $4\frac{1}{2}$ hours. At Mansfeld 6 to 7 cwt. of black copper are refined in $2\frac{1}{2}$ hours. At Atvidaberg charges of from 19 cwt. to $24\frac{1}{2}$ cwt. were refined in 4 to $4\frac{1}{2}$ hours with a blast pressure equal to $2\frac{1}{2}$ to $2\frac{2}{3}$ inches of mercury. The

fuel consumption averages, with charcoal, 50 per cent. of the weight of the refined copper.

Refining in reverberatory furnaces. This form of refining is employed for larger outputs and more impure coarse copper; it has the advantage of requiring less time, because the copper does not come into contact with the fuel; a larger proportion of copper is, however,

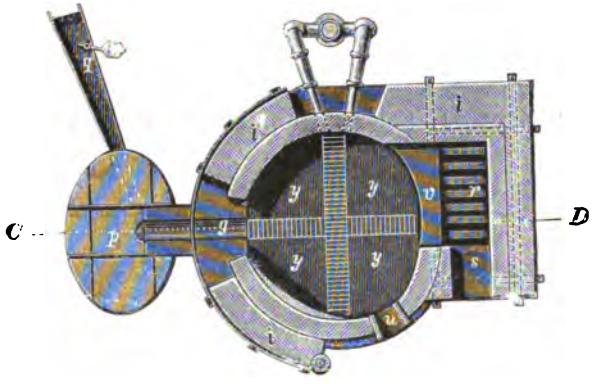


FIG. 114.

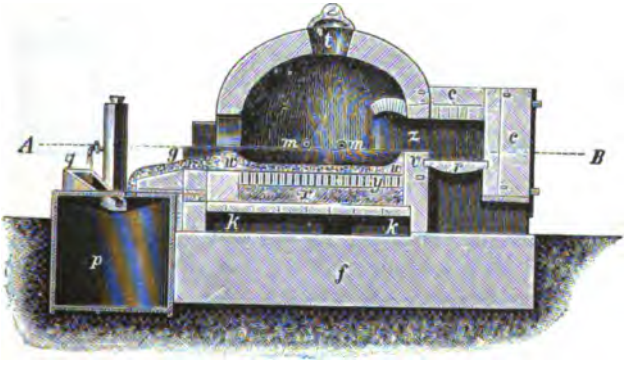


FIG. 115.

slagged off, as the oxide is not again reduced, as in the small hearth.

The reverberatory furnace with blast, the so-called *spleiss-furnace* is built like the German cupellation furnace. The bed consists of loam, quartz, or a brasque of charcoal dust. According to whether the refined copper is to be granulated or taken off in discs, a granulator or a number of rosetting wells or hearths are arranged in front of the furnace.

The construction of the *spleiss-furnace* used in the Harz is shown in Figs. 114 and 115. The foundation of the furnace is at *f*; *k* are

flues, about 12 inches square, for carrying off moisture; r is the grate (2 feet 6 inches wide by 5 feet 2 inches long), s is the fire door, v the fire bridge (15½ inches wide and 5 feet 2 inches long), z the fire space over the bridge, t an opening in the roof for admitting cold air, the highest point of the arch being 6 feet above the top line of the hearth m m. At x there is a layer of slag, 10 inches deep, on which rests a bed of bricks y, 6 inches deep, upon which lies the bed proper w, made of a mixture of charcoal dust and marl, 8 feet 9 inches in diameter. The retaining wall of the furnace is shown at i, g is the taphole and u the working door 15½ inches wide and 28 inches high; m m are the tuyeres. In order to granulate the copper, as is necessary

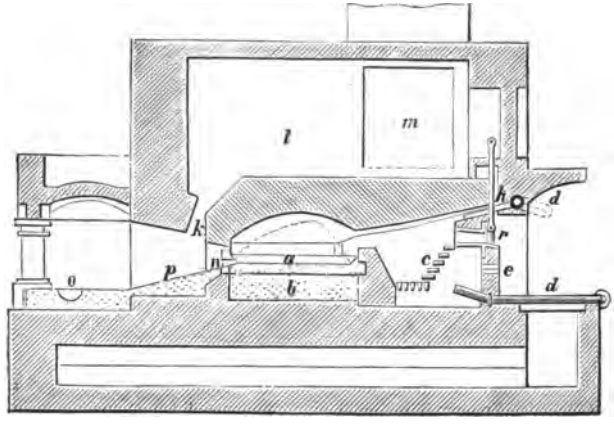


FIG. 116.

for the extraction of its silver in the wet way, it is run through an iron gutter lined with a brasque of charcoal breeze, into the granulator p where it meets a stream of cold water that enters through the gutter q.

The Hungarian furnace, as used at Schmöllnitz, is shown in Figs. 116 to 118. It has a step grate c arranged for burning wood, which is supplied with air both above and below the grate through the system of pipes d. The bed a, having an area of about 54 square feet, is prepared from a mixture of 50 parts of quartzose clay slate, 33 parts of talcose slate and 17 parts ground brick, which is stamped down upon a bed of charcoal breeze b. The working door is at f; g g are the tuyeres, one of which lies 5 inches and the other 6 inches above the bed, and both of which are inclined at an angle of 1°. The flues i i lead the products of combustion into the flue k and thence into the dust chamber l; out of these they escape by the

flue *m* to the stack. At *o o* are rosetting basins into which the refined copper is run over the slope *p* through the tap hole *n* in order to be rosetted.

The charge for this furnace may vary up to 3½ tons of coarse

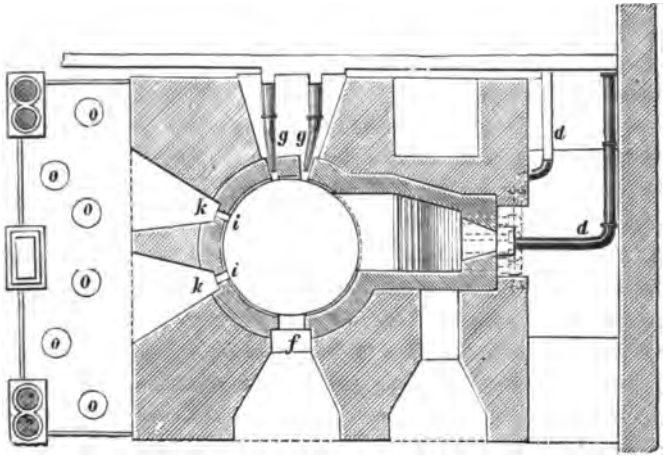


FIG. 117.

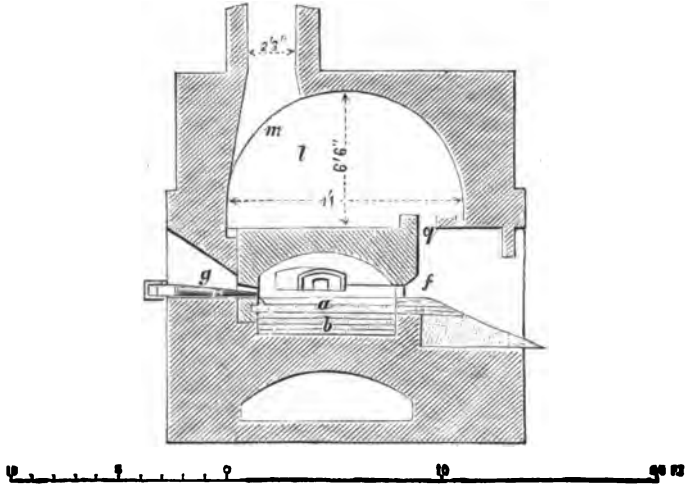


FIG. 118.

copper; it is charged through the working door in such a way that the flame can circulate freely between the pieces. Pure coarse copper melts more rapidly than when it contains arsenic, antimony or sulphur. The blast is usually not turned on until the charge is

melted, and is gradually increased as the temperature rises. The slag that forms is skimmed off from time to time. When the copper is found to be refined, it is either tapped into the small basins *o o*, and rosetted, or else is run into a granulator; in the latter case the copper must run in as thin a stream as possible and be brought into contact with a strong current of cold water to prevent explosions.

The chemical reactions are the same as in the small hearth. When very impure copper is treated the operation is prolonged, and a proportionately large amount of cuprous oxide is produced; this is reduced to the requisite extent by covering the metallic bath with charcoal, by poling, or by the addition of lead to the copper. In Hungary the excessive oxidation of the copper is prevented by stopping the blast as soon as fumes cease to be evolved from the bath of metal and only small quantities of red slag form, and completing the oxidation by means of the air entering from the grate. As in the small hearth, copper mica is dissolved by the addition of lead.

In Hungary, when the coarse copper contains much antimony and arsenic, reduction by charcoal and oxidation by the blast are alternately applied, until the above substances are almost entirely got rid of.

The time occupied depends on the size of the charge and the amount of arsenic and antimony present in the coarse copper; with 3-ton charges it averages 10 to 15 hours. The consumption of fuel also depends on the above considerations and on the nature of the fuel used; with coal it averages 30 to 40 per cent. of the weight of the coarse copper.

At Altenau in the Upper Harz, the bed consists of a mixture of clay and marl (111 cubic feet of clay to 7 cubic feet of marl), and will stand 3 or 4 charges, the first of 3 tons, the second of 53 cwt., the third of 47 cwt., and the last, if the bed still admits of it, of 2 tons. The first charge is worked off in 15 hours (of which 10 to 12 hours are occupied in melting and the rest in blowing), the second charge in 12 hours, and the third in 8 hours. After the third or fourth charge a new bed is put in. In the course of a year 340 tons of coarse copper were treated, producing 201 tons of granulated copper, 104 tons of ordinary refinery slag, and 33 tons of nickeliferous slag. The consumption of fuel was 84 tons of coal and 1475 billets of small wood. At Oker, where granulated refined copper was made from black copper, the coal consumption was 55 per cent. of the weight of the latter, the yield of granulated copper being 65 per cent. of the charge.

At the Stefanshütte in Hungary, 33½ to 56 cwt. of black copper

formed the charge; the furnace was warmed up for 48 hours; it was then fired for 12 hours till the copper was red hot, then for another 3 hours till it was melted down; the formation of slag went on for another 8 to 10 hours with repeated lowering of the temperature, and finally the over-refined copper was brought back to its proper condition by poling.

Refining in reverberatory furnaces with natural draught, as carried on, for instance, at Oker in the Lower Harz, is performed in furnaces of the English type, and is identical with the first period of refining it by the English method to be subsequently described.

The products of this method of refining (*gaarmachen*) are: refined copper, and slag known as *gaarkrätze*, "refinery dross," "refinery slag" or "rosette slag."

The refined copper contains, besides larger or smaller amounts of cuprous oxide, small quantities of foreign elements and metallic compounds. The composition of several varieties is shown by the following analyses:—

	Mansfeld.	Atvidaberg.	Lend (Salzburg). (with 1 per cent. copper mica.)
Cu	98·40	99·46	97·00
Fe	0·07	0·01	—
Pb	0·57	trace	0·70
Sb and As	—	—	1·10
Ni	0·45	0·11	0·46
Ag	0·02	0·06	—
Au	—	0·001	—
S	0·01	0·02	—

Other constituents not determined.

The impurities of various kinds of refined copper are as follows:—

	Stefanshütte.	Agordo.	Klausen.
As	0·13	0·64	0·059
Sb	0·08	0·04	0·057
Pb	trace	0·20	0·390
Fe	trace	—	—
Ni	0·29	—	—
Ag	0·011	0·10	0·077
Au	trace	—	—
S	—	0·04	—

This refined copper is either used for brass-making or is toughened to tough-pitch.

Refinery slags are mixtures of silicates of copper and iron with oxides of the various metals that had existed in the coarse copper, together with antimoniates, arseniates and sulphates of lead mostly. They consist partly of molten slags, partly of agglomerated masses. When they contain nickel and cobalt in workable quantities they are treated separately; otherwise they are added to the ore or the matte-furnace charges for the recovery of the copper they contain. Nickeliferous dross is smelted in shaft furnaces for coarse copper or, when it contains much arsenic and antimony, for Speiss. The copper obtained from this dross, known as *Krätz-Kupfer* ("dross-copper"), when scorified or refined, again produces dross in which the nickel and cobalt are concentrated. When this dross is smelted, a copper still richer in nickel is obtained, and by the repetition of these alternate smelting and scorification processes, copper rich in nickel, which is sold to nickel-works, is ultimately produced. Refinery dross may also be smelted with the addition of pyrites for a nickeliferous matte. Many works sell their nickeliferous dross direct to nickel smelters.

(*b*) *The Production of Tough-pitch Copper.*—The toughening of refined copper consists in a reducing fusion or, if it is still contaminated with foreign elements, especially arsenic and antimony, in an oxidising fusion immediately following the reducing fusion, and itself followed by another reducing fusion. The toughening furnace is similar to that used for refining coarse copper, except that the tuyere lies at a flatter angle of inclination (6° to 10°), and projects further over the edge of the hearth. Charcoal is the fuel used, the charge being 8 to 12 cwt. of refined copper. The fusion in the small hearth is rendered a reducing one by directing the blast not on to the bath of metal, but, by means of the low inclination of the tuyere, upon the charcoal; the latter is piled against the tuyere, whilst the pieces of copper are so placed as not to be caught by the blast. They accordingly melt in an atmosphere chiefly of carbon monoxide, in which the cuprous oxide is reduced by that gas and by contact with the glowing charcoal. After the copper has been melted down, the slag is skimmed off and a sample taken, either by means of the iron rod or as a dip-sample. If this shows the salmon-pink colour, satin lustre, and fibrous structure of tough-pitch copper, and the requisite softness and toughness when hammered out and when broken in the vice, it is ladled out. If, however, it still contains cuprous oxide (is still *dry*), which is shown by the ease with which the sample may be broken, and by the cubical or columnar structure and dark red colour of the fractured surface, the bath of metal is again covered with charcoal and the reducing fusion

continued. If the copper still contains impurities, an oxidising fusion must be maintained until these are removed and the cuprous oxide be afterwards reduced by a reducing fusion. In case of need, alternate oxidations and reductions are repeated until the copper is at tough-pitch. The tough-pitch copper is cast into moulds. As soon as they have set, the red-hot ingots (*hartstücke*) are hammered so as to remove the brittle crust of oxide of copper (*copper scale*) that will have formed upon them; this operation is known as *abpochen* ("pounding off").

At Schmöllnitz, about 8 cwt. of refined copper were toughened in about 3 hours with a loss of 1·28 per cent. and a charcoal consumption of 59·34 per cent.

In the Lower Harz, 5 cwt. used formerly to be toughened in 2½ to 3 hours, with a loss of weight of 2 to 3 per cent. and a charcoal consumption of 60 per cent.

2. *The Purification of Copper by combined refining and toughening in the Refining Hearth*

This operation is performed in the small hearth, the first portion being identical with that already described for refining coarse copper; when this stage has been reached oxidation is allowed to continue till the copper is over-refined, its condition being determined by a dip sample. Over-refined copper shows cubical or columnar structure and a dark red colour approaching to violet on the fractured surface. The oxidation when carried to this point, removes the foreign constituents. The copper containing cuprous oxide is now covered with charcoal and poled, whereby this cuprous oxide is reduced to metal. If a dip sample now shows the characteristic signs of tough pitch, the metal is ladled into moulds. If not, the blast is again turned on and oxidation continues till the copper is over-refined, when it is again poled under a layer of charcoal, and these operations are repeated alternately till the copper is at tough pitch.

The products of this process, which is no longer in use to-day, are besides tough copper, refinery slag and copper scale, which are added in ore, matte or coarse copper smelting.

3. *Refining of Copper (English process)*

Refining of coarse copper, in the English sense of the word which includes toughening, consists of an oxidising fusion of coarse copper, immediately followed by reduction of the cuprous oxide formed. Both operations are repeated until copper of the desired softness, toughness, and density are obtained.

The furnaces used for this operation are English reverberatory furnaces with a bed of quartz or sand, or, as in Wallaroo, of hollowed out sandstone, capable of holding from 1 to 15 tons of copper. The air needed for oxidation enters by the working doors as also through special openings at either side of the firebridge, the draught being produced by a stack at least 65 feet high. In many Russian works a blast is used, especially in cases where very mpure coarse copper has to be dealt with. The copper is charged from the floor level of the works and generally through a special woiking door in the side of the furnace. Exceptionally big lumps of native copper are at Lake Superior charged through the roof, which is then made removable in part. Where the copper is not charged in pieces, but in the form of powder, as for instance, the residues from the Ziervogel process at the Gottesbelohnungshütte at Mansfeld, which consist of cupric oxide, this is also dropped in through apertures in the roof. The refined copper cannot be tapped out, because it would partially set in the taphole, and, in case of obstructions in the latter, could only be removed with difficulty, whilst the stream would be so irregular that it could not be run into moulds of definite size. It has therefore to be ladled out and cast into moulds. The bed slopes from all sides towards the ladling door; the latter, which may also be used as the working door, is situated near the fluebridge end, so that cold air entering through it may pass straight into the stack and neither cool nor oxidise the molten metal. The furnaces may be fired by means of an ordinary grate or by gas (producer gas); the latter may be advantageously employed when the fuel (*e.g.* chips of wood in Sweden) is not suitable for burning on a grate. The best fuel is wood, as it evolves no gases containing sulphur which would affect the metal injuriously; where it is not to be obtained in sufficient quantity, coal burning with a smokeless flame is employed.

The bed of small furnaces is fired in one layer, in other cases in several, generally two. Usually a certain amount (about $\frac{1}{6}$) of fire-clay, or some slag is added to the quartz for making the bed; as the latter absorbs considerable quantities of copper, it is often saturated as far as possible with that metal before the furnace is actually put into operation.

Beds made of basic material present no special advantages in this process, because the copper to be refined is already tolerably pure, and antimony and arsenic are not removed from it more rapidly on a basic than on an acid lined bed.

The size of the furnaces must not exceed certain dimensions, because it is difficult to keep large quantities of copper

at the proper pitch during the long period occupied by the ladling.

The smallest charges are those worked in the Siberian refinery furnaces using blast, namely 1 to 2 tons. Medium sized furnaces take 3 to 7 tons, large ones 8 to 10, and the largest 12 to 15 tons. At

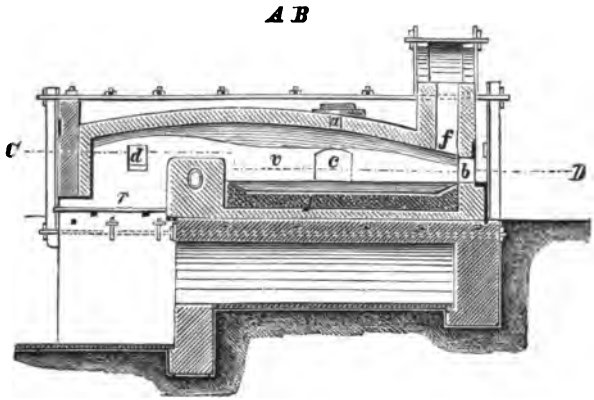


FIG. 119.

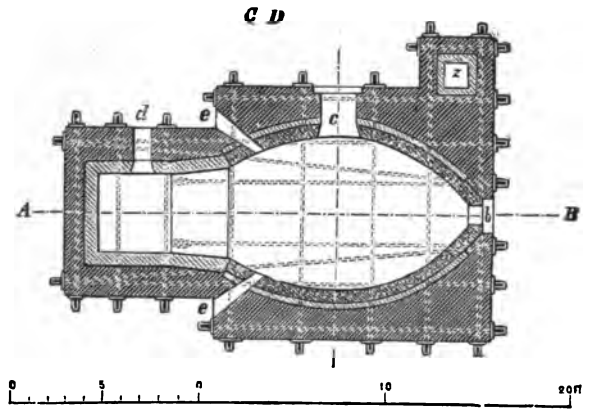


FIG. 120.

Wallaroo 10 ton furnaces, and at the Orford works 15 ton furnaces are in operation.

The construction of refinery furnaces is shown by three examples taken respectively from Mansfeld, Lake Superior and Pittsburg.

The Mansfeld furnace is shown in Figs. 119 and 120. The charge here does not consist of coarse copper, but of the pulverulent residues from the Ziervogel process of silver extraction, consisting of cupric

oxide with some oxide of iron, which is charged mixed with a sufficient proportion of charcoal for its reduction, the charge being 5 to 7½ tons. This is reduced in the first part of the process and then immediately refined.

In the figures, *v* is the furnace body, *a* the aperture for charging, *f* the bed made of quartz to which a little slag has been added, *r* the grate worked with a clinker bed, *d* the firedoor, *f* the flue, *c* a door

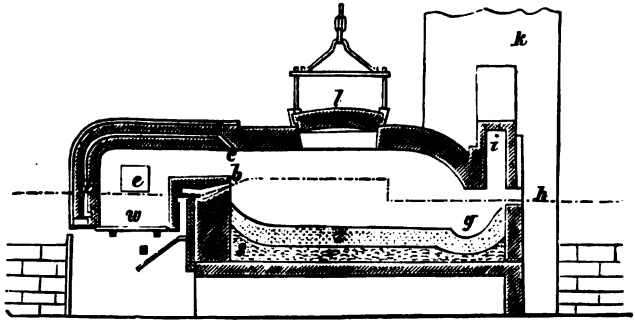


FIG. 121.

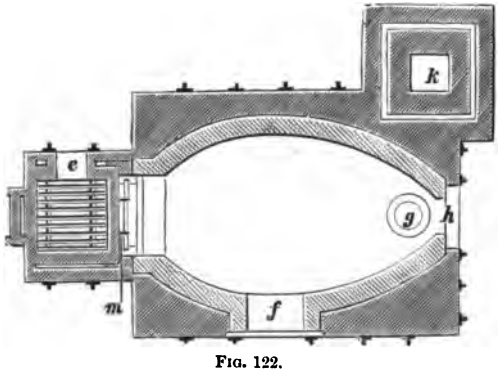


FIG. 122.

for charging big lumps if required, *b* the working door, through which the copper is also ladled out. At *e e* there are two channels for the admission of air to the furnace, this being regulated by more or less blocking them with bricks.

Figs. 121 and 122 represent a refining furnace such as is used at the Lake Superior Refining Works for native copper. As is shown in the vertical section Fig. 121, the roof is kept parallel with the bed till close to the fluebridge, and is then drawn in suddenly. This makes it more easy to arrange suitably in the furnace big blocks of copper, charged in through the door *f*. The largest pieces are lowered in by

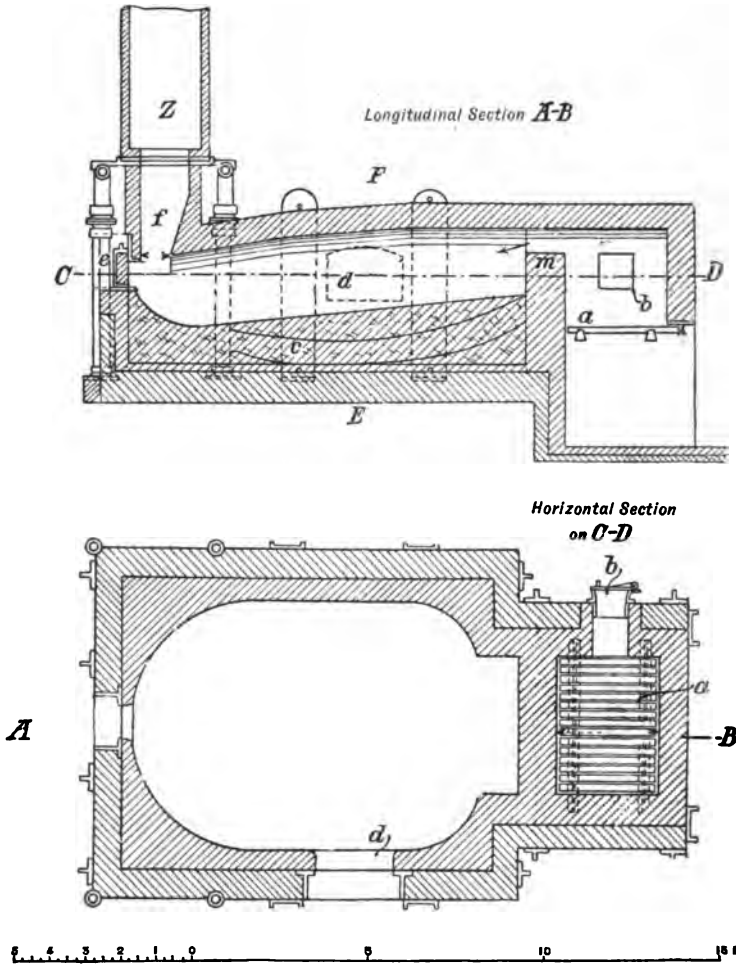
means of a crane, after the shifting portion *l* of the roof has been taken off. The charge is from 3 to 10 tons, but has recently been still further increased. The bed, 14 feet long, is 10 feet wide in the middle, and 2 feet 4 inches at the ladling door. It is composed of a layer of sand rich in iron, 8 inches deep, *s*, upon which is a layer of quartzose sand *z*, which is saturated with copper before operations commence. The total thickness of the bed at the firebridge is 3 feet 3 inches; *g* is the sump or well, *i* the flue, *k* the stack, *e* the firedoor, *w* the grate. The air enters the furnace through flues in the brickwork *b* and *c*, which can be controlled by valves.

A copper refining furnace used at Pittsburg, Pennsylvania, is shown in Figs. 123 to 125. In these *a* is the grate, *b* the firedoor, *m* the firebridge, *c* the bed, *d* the charging door, *e* the working and ladling door, *f* the flue.

A gas-fired furnace is employed at Stadtberge in Westphalia, a regenerative Siemens gas furnace at Atvidaberg in Sweden; this latter very closely resembles that used for steel making,[1] only the copper is not tapped but ladled out. Such a furnace, full working drawings of which may be found in Peter's work,[2] only takes $2\frac{1}{2}$ tons of coarse copper. The gas is produced from chips of wood. The general arrangement of the furnace is shown in Figs. 126 and 127. *GG'* are the regenerators filled with firebrick, through which the gas alternately enters the furnace, L L' the regenerators for the air. V_3 are the gas-, V_2 the air-reversing valves. *H* is the furnace body, Q the quartz bed, E the charging door, S the working and ladling door. The air needed for oxidation is admitted either through separate openings, or else some of the air current required for combustion is diverted into the furnace. In general, for copper refining, grates are preferable to gas firing especially with regenerators, because these are apt to get blocked up, and because of the difficulty of introducing into the furnace sufficient air for oxidation.

The method of refining depends solely on the composition of the coarse copper, as regards principally the amount of sulphur, arsenic and antimony present. Thus with copper that does not contain these elements like Lake Superior copper, it is merely a matter of getting rid of a certain amount of gangue and a little iron, and of getting dense castings of a specific pattern. With copper free from sulphur, the operation of refining is considerably shortened by the omission of the so-called *braten* ("boiling up") and *dense-poling*, whilst it is greatly prolonged in the case of coarse copper containing much

[1] *Allgemeine Hüttenkunde*, pp. 241 and 452.
[2] *Op. cit.* 1895, p. 510.



FIGS. 123 and 124.

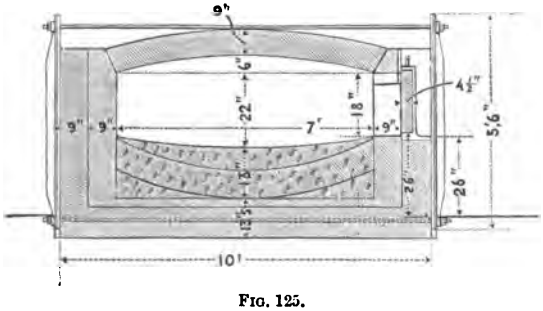


FIG. 125.

sulphur and contaminated by considerable quantities of foreign metals (Ni, Co, Bi, As, Sb).

It will be advisable to take, as the starting point for a study of

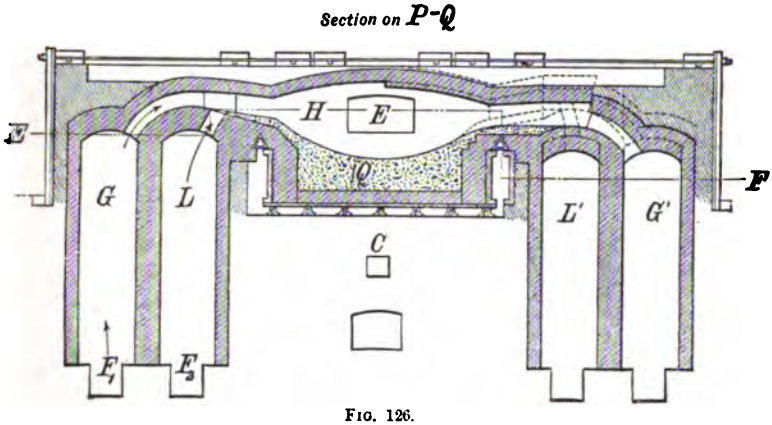


FIG. 126.

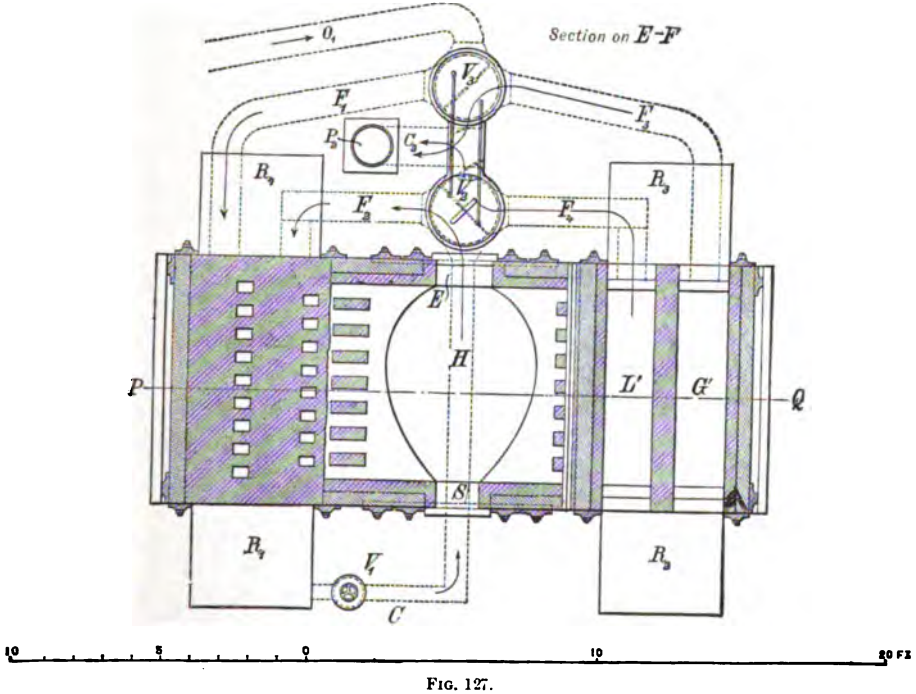


FIG. 127.

refining, such a coarse copper as is produced in German, Austrian, English and Swedish works, containing a certain amount of sulphur

and a small proportion of arsenic. With charges of 5 to 7 tons, and when burning coals giving a long flame on an ordinary grate, the time occupied in refining will be from 18 to 24 hours, according to the degree of purity of the metal.

The coarse copper must be so charged that the flame can readily pass round each individual piece; this operation takes about an hour for 5 to 8 tons of coarse copper. With sufficiently pure copper under normal conditions, the following successive stages of the process may be distinguished:—

1. Fusion.
2. Scorification (*Verblasen*).
3. Boiling (*Braten*).
4. Dense-poling (*Dichtpolen*).
5. Tough-poling (*Zähpolen*).

The fusion is performed for the purer kinds of coarse copper, with doors closed down and luted with clay so as to exclude all air. With less pure kinds it is advisable to allow air to enter either through the flues for air admission or by partially opening the working doors, so as to partially oxidise the foreign elements at this stage; a slag rich in cuprous oxide is thus formed which exerts an oxidising action on the impurities. The fusion stage takes 6 or 7 hours for 6 to 8 ton charges.

When the coarse copper is melted down, the air flues are opened, or if a blast is used, this is turned on, when the period of scorification commences. Zinc, lead, arsenic and antimony are partly volatilised, partly oxidised; sulphur escapes as sulphur dioxide; iron, nickel, part of the zinc, and a portion of the copper are oxidised and slagged off, the requisite silica being derived from the lining of the bed. The slag also takes up all other bodies that come to the surface of the bath of metal. Besides the oxygen of the air, cuprous oxide also acts as an oxidising agent, dissolving in the molten metal and then giving up its oxygen to the foreign elements present. The slag is repeatedly skimmed off the bath of molten metal so as to give the air free access to the latter.

After 2 to 2½ hours, with a 6 to 8 ton charge, the formation of slag almost ceases, whilst an evolution of bubbles from the molten metal becomes noticeable. This is the beginning of the boiling (*braten*) stage. Cuprous oxide is now acting violently upon the still undecomposed sulphide of copper, producing metallic copper and sulphur dioxide. This latter escapes in bubbles, and at first, with many kinds of copper, causes the production of copper rain, and afterwards with all kinds violent foaming of the bath which may go as far as ebullition

of the latter. This is the origin of the German term *braten* (= frying) for this stage, here translated by "boiling." The copper rain, described under refining, page 173, does not appear with all kinds of copper, but generally with the purer kinds of coarse copper that still contain a good deal of sulphur, especially when, after the slag has been skimmed, the temperature falls. Dip samples taken during this stage in an iron spoon show a foam-like mass of copper. As the operation advances and the formation of bubbles slackens, the samples become denser, and as they cool crater-like elevations form on the surface, through which the sulphur dioxide breaks out. When the formation of bubbles has still further stopped, these elevations disappear, and the sulphur dioxide can no longer break through the setting surface of the samples, but simply raises it. When the ebullition is over, the copper still retains a certain quantity of sulphur dioxide, which it only gives off during poling. A sample taken at this period only shows a rising of the upper face, and, when broken in the vice, a number of little cavities on the fractured surface. At the end of the boiling stage, which lasts 3 to 4 hours, the copper is in the dry state. In addition to sulphur dioxide it still retains considerable quantities of cuprous oxide.

To remove the sulphur dioxide, the copper bath is now submitted to an operation of poling, called by the Germans dense-poling (*dichtpolen*); for this purpose a pole of green wood, secured outside the furnace, is thrust with the butt end downwards into the molten copper down to the bed of the furnace. The portion of the wood immersed in the hot fluid mass there undergoes dry distillation; it evolves steam, hydrocarbons, hydrogen and carbon monoxide, which cause violent agitation and bubbling up of the bath of metal. The absorbed sulphur dioxide is thus expelled, like carbon dioxide is from a glass of beer by shaking the latter. By the contact of the cuprous oxide with the reducing gases evolved from the wood, the former is reduced to the metallic state, whilst, on the other hand, the molten metal tossed up into the air is at the same time exposed to oxidation. The complete removal of the sulphur dioxide is indicated by the smooth surface of the dip sample. After this, which takes place in two or three hours, the reduction of the cuprous oxide is proceeded with, or, if the copper still contains foreign elements, the air is allowed to oxidise the surface of the molten metal for some time longer. The sample, which should be fixed convex side upwards in the vice, has a brick-red fracture and shows a structure at first columnar but afterwards cubical as the oxidation of the copper advances; at a still further stage the brick-red colour has a strong

violet tinge. The degree to which the metal has to be oxidised depends on its purity.

The reduction of cuprous oxide is generally performed under a cover of charcoal or anthracite by means of further poling, known in Germany as "tough-poling" (*zäh-polen*). A fresh pole of wood is inserted into the covered bath as in the last operation. The reducing gases produced by the dry distillation of the wood, together with the contact of the copper with the covering of coals, promoted by the ebullition of the bath, reduce the cuprous oxide to metal. The author has repeatedly observed that the gases generated can by themselves effect this reduction, the process having been carried on for a considerable time, during his presence in the Caucasus, without the covering of charcoal.

As this reduction proceeds, the copper becomes softer and tougher. In order to judge of the changes taking place in the molten bath during this poling, samples must be taken continually; they are dipped out with a small spoon made of iron plate, cooled in water, fastened in a vice, and broken. The cubical structure of the fracture gradually passes successively into a coarse columnar, a fine columnar, a coarsely fibrous, and, lastly, into a finely fibrous structure. Concurrently with these changes in structure the colour changes from violet to brick-red, yellowish red, and, lastly, to a fine salmon pink. The lustre, which was at first wanting, appears as the density increases, and is at last vividly silky. At the same time, the copper becomes dense, and so soft as only to be broken with difficulty in the vice. In the latter stages the tenacity is also tested by forging a sample into a square bar, and twisting this into a spiral, when no fissures should show on the edges. Another sample is hammered out into a thin sheet, which should only break after being repeatedly bent backwards and forwards. If these qualities are wanting in the copper after the poling is finished, it still retains some impurities. If these can be removed by further oxidation, as in the case of nickel (antimony, arsenic, bismuth and tellurium are more difficult of removal), the metal is again oxidised and then poled. Generally speaking, alternate reductions and oxidations are employed until the copper shows the requisite qualities, great softness and toughness, highly granular fracture, rose pink colour and satiny lustre.

Arsenic and antimony cannot be completely removed by oxidation alone. In order to get rid as thoroughly as possible of these substances, lead or, at the commencement of the process, pure white metal, is added to the bath of molten copper. Arsenic is not, however, completely removed even by this method; the best plan is

therefore to get rid of the arsenic in the calcination and smelting operations that precede the production of coarse copper.

This tough-poling lasts generally one hour, but may take several, if oxidation and poling have to be repeated. Many kinds of copper have, as previously stated (p. 2), the property of absorbing certain of the gases, such as hydrogen and carbon monoxide, evolved during poling, and of thereby becoming porous. According to Hampe,[1] hydrocarbons, such as ethane and methane, are not absorbed by copper, but are in part dissociated at the temperature of molten copper, carbon being separated and hydrogen absorbed by the copper. Sulphur dioxide, too, can render copper porous, this gas being produced by the action of cuprous oxide formed by the oxidation of the copper during pouring upon sulphide of copper remaining undecomposed. Porous copper is not suitable for rolling or hammering, but can be employed in brass-making; the above-mentioned gases must therefore be eliminated before or during casting from copper intended for rolling. The method most used is the addition of a small quantity of lead before pouring. Probably the lead, which diffuses uniformly throughout the bath, expels the gases by being itself for the most part volatilised. Others ascribe its action to its oxidation and combination with cuprous oxide, so that any sulphide of copper present can no longer be decomposed by the latter. Small quantities of lead that remain in the copper, as already stated, do not affect its behaviour in the rolls. Copper, on the other hand, that is to be used for brass-making (called in Germany *Gussrafinad*) may not contain any lead, but the porosity in this case does no harm.

Like lead, water vapour and carbon dioxide have the power of expelling the absorbed gases from copper. Hesse leads carbon dioxide into closed moulds, whereby the gases are expelled. According to Stahl,[2] copper containing small quantities of arsenic does not absorb any gases, and as arsenic can be contained up to 0·4 per cent. in copper without impairing its properties, it forms, according to Stahl, a means for preventing the copper from becoming porous.

Another method of preventing it, is by reducing the cuprous oxide instead of by poling, by substances that do not evolve any gas, such as phosphorus, phosphor-bronze and manganese-bronze. Phosphorus acts by reducing cuprous oxides to the metallic state, and becoming itself oxidised to phosphorus pentoxide, which combines with another portion of the cuprous oxide to form phosphate of copper; this floats

[1] *Zeitschrift für Berg.- Hütten- und Salinenwesen im Preuss. Staate*, 1873, 21, 275. *Chemiker-Zeitung*, 1893, 17, No. 92.

[2] *Inaugural Dissertation*, Tübingen, 1886.

on the surface of the bath, and can be again reduced to phosphide of copper by the action of the layer of coal. Phosphor-bronze (a compound of phosphorus and copper) is to be preferred to free phosphorus. In the case of manganese bronze (an alloy of copper and manganese) the manganese acts as the reducing agent.

As soon as the copper has attained the above-described properties, ladling must be commenced without delay. Many kinds of copper lose their valuable properties through too long poling, whilst others become porous. Many, however, as the author has proved by long experience, remain unchanged. Copper that has lost its good qualities through too long poling is known as *over-poled* copper.

The loss of the valuable properties of copper through over-poling was, in accordance with Karsten's views, ascribed to the absorption of carbon by the fluid metal, up to the year 1874, when Hampe showed that copper cannot absorb carbon, and assigned the correct reason, namely the reduction of certain oxides and salts contained in certain qualities of copper, as has already been fully explained. (See page 5.)

Over-poled copper must be oxidised again, and then poled back to the right pitch, as also must copper that has been rendered porous by too long poling, and is free, according to Stahl, from arsenic and lead. The copper is ladled out by means of wrought-iron ladles daubed with lime or clay. The moulds into which the copper is cast are made of cast-iron or copper.

The cast-iron moulds are in the form of frames standing on a cast-iron plate from which they can be lifted. Copper cast in these moulds becomes porous where it is in contact with the bottom plate from some unknown cause, though it has been assumed that the bottom plate becomes coated with a film of oxide, which by its action on any sulphide of copper remaining undecomposed, evolves sulphur dioxide, which makes the metal porous. For this reason, a thin layer of copper is first poured on to the bottom of the mould, and allowed to cool to below redness; the rest of the ingot is then poured to the required depth on to the copper bottom plate thus formed. The porous plate is returned to the furnace for refining.

When copper moulds are used, the copper shows no porosity at its contact with the mould; hence these are used for casting small ingots. They are set over a tank of water, and can be revolved round a horizontal spindle, parallel to their shorter side, so that when the copper ingot has cooled to a certain degree, it can be tipped into the water. In order to be able to divide the ingots readily, they are deeply notched, the moulds having corresponding ribs. Figs. 128 to

130 show the arrangement of the moulds, Figs. 131 and 132 the shape of the ingots, the latter being the English shape. The copper moulds are made by means of a special press shown in Fig. 133; the fluid copper is poured into the box *f*, and before it sets the stamp *c* is pressed into it, producing a mould of the required shape.

Whilst the copper is being ladled out, samples must be taken from

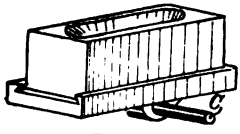


FIG. 128.

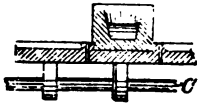


FIG. 129.

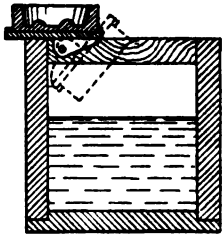


FIG. 130.

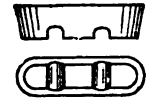


FIG. 131.

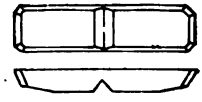


FIG. 132.

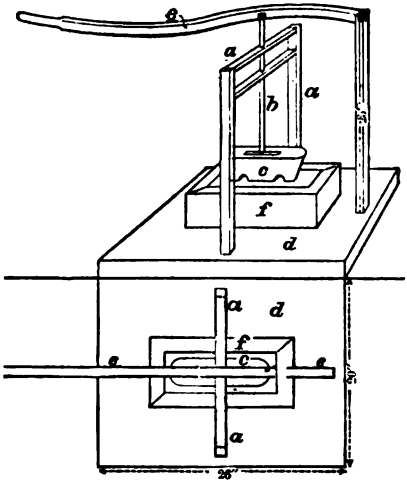


FIG. 133

time to time. Should these indicate any oxidation of the copper, the metal must be brought back to its normal pitch by poling. According to the size of the charge, ladling and casting may take one or several hours.

The consumption of fuel depends on the purity of the copper, the size of the charge, and the quality of the fuel; it varies between 33 per cent. and 65 per cent of the weight of the charge. With the

large 12 ton charges in the United States, it is taken at 30 to 33 per cent. of the product (about 94 or 95 per cent. of the copper contents of the coarse copper).

A refining furnace can work for 3 weeks up to several months (4 in the Caucasus) before a new bed needs to be put in. At Wallaroo where it is hewn out of solid sandstone and repaired with clay, it lasts for a number of years.

The products of the refining process are refined, *tough-pitch* copper or *tough-cake* (the Germans distinguish between *guss-raffinad*, refined copper for brass making and *walz-raffinad*, refined copper for rolling) and slags known or refinery dross or refinery slag.

Copper to be used for electrical work may not contain more than traces of impunity because these diminish its conductivity. The best copper for this purpose is Lake Superior copper, the so called Lake copper, and copper prepared by electrolysis.

The impurities contained in various kinds of refined copper are shown in the following table :—

	Chili.	Spain.	Australia (Burra-Burra.)	Lake Superior.	Caucasus (Kedabeg).	Ural. Nishni-Tagilsk.	England. Best selected.	England. Best selected.
Fe	0·08—1·64	0·35	—	0·0077	0·0080	0·0034	0·10—0·15	0·10
Ni, Co	—	—	—	0·0146	—	—	—	—
Ag	—	—	—	0·0289	0·1613	0·0032	—	—
As	trace—0·5	0·25—3·31	0·02	—	0·0151	0·0002	—	—
Sb	trace—0·5	trace—0·70	—	trace	0·0087	0·0042	—	0·01
Bi	trace	trace—0·04	—	—	—	—	—	—
Pb	—	—	—	—	—	—	—	—
Sn	—	—	—	—	—	0·0036	—	—

The composition of Mansfeld refined copper is shown by the following analyses, No. I. and II. being *Guss-Raffinad* for brass making, and No. III. and IV. *Walz-Raffinad* for rolling or hammering :—

	I.	II.	III.	IV.
Cu	99·442	99·512	99·340	99·198
Ag	0·026	0·028	0·023	0·014
Pb	0·006	0·042	0·204	0·206
Ni, Co	0·317	0·279	0·298	0·467
As	0·025	not determined	0·030	0·061
Fe	0·024	0·037	trace	trace
S	—	—	not determined	not determined

The composition of refinery slag varies greatly with the purity of the coarse copper, and the stage of the refining at which it is obtained; it consists of a mixture of silicates and metallic copper.

The following is an example of a Welsh refinery slag:—

Silica	47·4
Cuprous oxide	36·2
Ferrous oxide	3·1
Nickel oxide	0·4
Tin oxide	0·2
Alumina	2·0
Lime	1·0
Magnesia	0·2
Metallic copper	9·0

In order to recover the copper, it is added to the ore or matte furnace charges, or if it contains a workable amount of nickel, treated separately for nickeliferous copper.

The following are examples of copper refining:

At Kedabeg in the Caucasus, the author saw refining performed in small furnaces supplied with blast—so-called Siberian furnaces, wood being the fuel used. The charge was 80 to 90 pood[1] of coarse copper, and the time occupied 8 hours, three charges being worked off in 24 hours. Of the time occupied for one charge, ½ hour was consumed in fettling and charging the furnace, 2½ hours in the fusion, 3½ hours in the scorification and boiling, and 1½ hours in poling. The fuel used in 24 hours was 1¼ cubic fathoms of wood. Each 100 pood of coarse copper yielded 82 pood refined copper and 25 pood refinery slag containing 30 to 50 per cent. of copper. The composition of the copper is shown in the following analyses:—

	I.	II.
Cu	99·6900	99·6700
Au	0·0067	0·0066
Ag	0·0877	0·0958
Pb	0·0110	0·0092
Fe	0·0350	0·0273
Zn	0·0731	0·1043
Ni	0·0057	0·0083

Copper intended for the Asiatic markets must show exteriorly a fine rose pink colour to suit their tastes. This is obtained by mixing

[1] One pood = 36·1141 lbs. avoirdupois.

wood tar with the water into which the copper is thrown after it has set in the moulds. A refining furnace lasts 4 or 5 months before it needs re-building.

The ores from Lake Superior which consist of native copper and a little cuprite are smelted in refinery furnaces and immediately refined. They are treated on Lake Superior, at Detroit, Hancock, and Pittsburg.[1] They average 70 to 80 per cent. of copper and are obtained by the mechanical treatment of the very low grade ores, the dressed material being known as *mineral*. It is either in larger lumps (known as *barrel work*) of native copper containing 96 to 97 per cent. of copper, sandy ores (mineral) from the steam stamps and dressing floors, with 80 to 85 per cent. of copper, or slimes with 30 to 40 per cent. of copper. The refining furnaces have already been described. The charge is from 5 to 12 tons. The largest pieces are charged first, then those of smaller grain, and the finest slimes last; some slag containing 25 to 30 per cent. of copper is added, and from 6 to 8 per cent. of limestone. As the ores are free from sulphur and other injurious impurities, the refining proper takes a correspondingly short time, and consists in scorification followed by poling. The fusion lasts 12 hours, after which slag is skimmed for another 4 to 5 hours. The scorification is continued till the copper is quite dry, greatly assisted by a method of stirring the bath known as *flapping*, and takes from ½ to 2 hours. The poling takes 2 hours, and casting the refined copper takes 2 hours more. For the production of 132½ cwt. of refined copper, 72½ cwt. of coals are consumed.

The copper refinery slags are smelted for copper in a shaft furnace 11 feet high with the addition of 8 to 9 tons of lime to each 20 tons of slags.

Eggleston (*loc. cit.*) gives the following percentage determinations of the impurities in Lake copper; it is distinguished by its high electrical conductivity, and is only equalled in this respect by copper prepared by electrolysis:—

	I.	II.	III.	IV.	V.	VI.
Fe	—	—	0·005	—	0·03	0·05
Ni	—	0·002	0·003	0·003	—	—
Co	—	—	—	—	—	—
Ag	0·030	0·030	0·030	0·030	0·070	0·04
O	0·280	0·280	0·190	0·220	0·370	0·20

[1] Eggleston, *Eng. and Min. Journal*, 33, pp. 167, 183, 196, 209.

In the Gottesbelohnungshütte at Mansfeld, the residues from the Ziervogel silver extraction process, consisting chiefly of cupric oxide and containing 75 per cent. of copper, are reduced in the refining furnace mixed with coal, and then refined. The oxide is mixed wet with 10 per cent. of coal and then dried; the charge for the above described furnaces consists of 4 to 5½ tons of residues. The operation of refining proper proceeds rapidly here because foreign substances are volatilised and slagged off in the course of the reduction and fusion; accordingly there is neither scorification nor boiling. In 8 hours, reduction, fusion, and slag formation are complete, and after the slag is skimmed off, dense-poling follows, taking 2½ to 3 hours, and tough-poling, taking 1 hour. The ladling of the copper into moulds takes 2 hours. After the furnace has stood empty for from 2 to 4 hours, during which time the bed is fettled, a fresh charge is put in. When *guss-raffinad* for brass making, which may be porous and contain a certain quantity of oxide of copper, is being made, dense-poling takes a correspondingly shorter time than when *walz-raffinad* is to be produced; to the latter a little lead is added. The fuel consumption is about 45 to 50 per cent. of the residues treated. A furnace campaign lasts 3 to 4 weeks. The refinery slags are smelted for coarse copper in shaft furnaces, this being worked into blister copper in *spleiss* furnaces, and then refined. The *spleiss-furnace* skimmings retain the nickel that was in the copper, and are accordingly smelted with pyrites in shaft furnaces for nickel matte. The total yield of copper, including the slag products, is 99·4 per cent.

Formerly Ziervogel residues used to be treated at Mansfeld by fusion for coarse copper in shaft furnaces, the copper being afterwards refined. The charge was 5 to 5·7 tons; charging took 1 hour, fusion 6 to 7 hours, scorification 2 to 2½ hours, boiling 3 to 4 hours, dense-poling 2½ to 3 hours, tough-poling 1 hour, ladling out 2 hours. The product was 80 per cent. of refined copper and 20 per cent. of slags.

Mansfeld refined copper, produced by direct treatment of Ziervogel residues in 1880 showed the following impurities:—

	I.	II.
Ag	0·028 to 0·030	0·016 to 0·020
Pb	0·043 „ 0·103	0·134 „ 0·259
Fe	0·025 „ 0·132	0·019 „ 0·024
Ni	0·239 „ 0·275	0·101 „ 0·144

At Oker, argentiferous coarse copper is refined for the production of anode-plates for the electrolytic separation of copper and silver.

The refining furnace is similar to that used at Mansfeld. The charge is 6 or 7 tons (generally 4½ tons coarse copper and 1½ to 2 tons anode residues from electrolysis or foreign copper). The fusion lasts 6 to 7 hours, scorification 4 hours, boiling 2 to 3 hours, dense-poling 1 hour, intermediate-poling 1 hour, tough-poling 1 hour, and ladling out 1 hour. With charging and fettling the furnace, the entire operation lasts 24 hours. The fuel consumption is 50 to 54 per cent. of the weight of the charge. The output is 89 to 90 per cent. of anode plates containing 98·5 per cent. of copper.

II. Extraction of Copper by Wet Methods

Wet methods are employed for ores so poor in copper that extraction in the dry way would be no longer profitable. Under favourable circumstances they can be applied to ores with only ¼ to 1 per cent. of copper. They are also used for the extraction of copper from metallurgical products containing gold and silver.

Their principle consists in getting into aqueous solution by means of suitable solvents, the copper which must exist in some combination suitable for solution, and of precipitating it from these solutions by means of suitable precipitants. The copper precipitate is refined in the dry way. If the copper is not present in the ores or metallurgical products in a form suitable for solution, it must first be got into such form.

The ores, from which copper is to be extracted in the wet way, contain it in the form of oxide, carbonate, sulphate or sulphide; phosphates and arseniates are so rare that they are only exceptionally treated by wet methods. From all these ores except the sulphides, the copper can be dissolved with sufficient rapidity by the aid of cheap solvents. Ores, on the other hand, that contain copper as sulphide, only admit of very slow and imperfect extraction by the aid of a cheap solvent (ferric sulphate); the energetic solvents, such as aqua regia, nitric acid, chlorine and hot concentrated sulphuric acid, are too dear to be applicable on a large scale. It is therefore necessary to transform the sulphide of copper into some form suitable for solution by cheap solvents such as water, hydrochloric acid, sulphuric acid or solutions of metallic chlorides.

We have therefore to consider separately:

1. The extraction of copper from ores, that contain it as oxide or carbonate.
2. The extraction of copper from ores, that contain it as sulphate.
3. The extraction of copper from ores, that contain it as sulphide.

In all these cases the copper is brought into solution as a sulphate or a chloride, and precipitated from solution by means of iron as metallic copper, or exceptionally by sulphuretted hydrogen as sulphide, or by lime as sub-oxide or hydrated oxide.

1. THE EXTRACTION OF COPPER FROM ORES THAT CONTAIN IT AS OXIDE OR CARBONATE

Cupric oxide only occurs exceptionally in sufficient quantity to form the object of a wet process. Azurite and malachite are much more abundant. For a while phosphate of copper together with malachite was the object of a wet extraction process at Linz on the Rhine.

a. The solution of the Copper. From the above combinations copper can be dissolved by means of sulphuric acid, hydrochloric acid, ferrous chloride, ammoniacal compounds, hyposulphite of soda and ferric sulphate. Of these solvents, only sulphuric acid, hydrochloric acid and ferrous chloride have been employed practically; the others have only been used experimentally and are in part too slow and imperfect in their action, and in part too dear.

Sulphuric and hydrochloric acids act very energetically; their applicability depends entirely on their price. If it is low, they should be used in preference to the much slower-acting ferrous chloride. When there are Leblanc soda works near the smelting works, the employment of hydrochloric acid is to be recommended. Ferrous chloride has found but limited application and with variable results. In the United States and in Siebenbürgen a mixture of green vitriol and common salt, in which ferrous chloride is the active solvent, has been employed (Hunt-Douglas process). More recently in the United States, sulphuric acid, to which ferrous chloride is added after leaching, has been used instead of ferrous chloride (New Hunt-Douglas process).

A necessary condition for the employment of acids is that the ores shall not contain in notable quantity other bodies, especially carbonates, soluble in acids. Other carbonates than those of copper are also prejudicial to the employment of ferrous chloride.

Lixiviation with Sulphuric Acid

Sulphuric acid is either used as such, or else sulphur dioxide, nitrous fumes and water vapour are allowed to act on the ores.

When liquid sulphuric acid is used (as is done when sulphuric acid chambers exist in the neighbourhood of the works), vessels of

sheet lead supported by wood, or of acid proof stone, are used; on a smaller scale stoneware vessels may also be used. Cupric oxide, azurite, malachite, and arseniate of copper dissolve readily, phosphate of copper with rather more difficulty. Cuprite is best left exposed to the air for some time after being moistened with acid, whereby it is transformed into cupric oxide. At Stadtberge in Westphalia and at Linz on the Rhine, ores containing 1 to 2 per cent. of copper used to be sulphated by means of sulphur dioxide, water vapour, and nitrous gases, and then lixiviated. At Stadtberge the ores were azurite and malachite disseminated through quartzose schist, at Linz, at the Stern works, copper carbonates and phosphates. The leaching vessels were tanks of brickwork, 3 feet 1 inch deep. Above the bottom proper these had a false bottom or grating made of acid proof material (firebricks at Stadtberge, basalt columns at Linz) supported by bricks on edge. The ores were piled up on this grating, the gases being conducted underneath it. The latter were respectively generated by roasting iron pyrites in shaft furnaces and zinc blende in muffle furnaces, and by treating Chili nitre with sulphuric acid. The sulphur dioxide, nitrous fumes, and water vapour together formed sulphuric acid which converted the copper compounds into sulphates. After 8 to 10 days the copper sulphate was dissolved out by means of water or of the acid mother liquors left after precipitating the copper. The leaching was, as should always be done, so conducted that fresh water or the copper-free mother liquor was allowed to attack the most completely exhausted ore, whilst the almost saturated solution was run on to fresh ore until it was fully saturated (22° to 26° B.). The liquor that drained away ran into receivers, whence it was again pumped on to the ores. This process, which extracted the copper down to $\frac{1}{4}$ per cent., has long ago been abandoned. In Stadtberge sulphuric acid was replaced by the cheaper hydrochloric acid as long as the supply of oxidised ores lasted.

Lixiviation with Hydrochloric Acid

Hydrochloric is preferable to sulphuric acid, because it is less apt to form basic salts than the latter (ferric sulphate when exposed to the air is decomposed into basic sulphate of iron and free sulphuric acid) and therefore yields solutions that contain but little free acid, and which accordingly require less iron for the precipitation of the copper than do solutions containing sulphate of iron. On the other hand it attacks oxide of iron more energetically than does sulphuric acid, and is therefore less suitable than the latter acid for treating ores that contain much ferric oxide.

It was formerly used with advantage at Stadtberge to extract copper from the above described ore containing ½ to 2 per cent. of metal.[1] The leaching vessels were rectangular tanks of wood 4 feet 1½ inches high, packed in a bed of clay 1 foot 1 inch thick, and fitted with a grating of wooden bars, upon which the ores were piled. The first tanks held 29 tons of ore, but those erected afterwards had a capacity of 90 tons. All the tanks were situated on one level. The leaching was methodical, ores nearly free from copper being treated with fresh hydrochloric acid of 12° to 13° B., as obtained from soda works, whilst fresh ore was treated with partially saturated solution until the latter was fully saturated, which took place at 19° to 20° B. The various solutions were allowed to remain 12 hours in each tank, the saturation point being reached in 10 to 12 days. The solution was circulated by means of pumps and bucket-wheels. After the solution had percolated through the ores, it ran out through a plug hole to which the bottom of the tank inclined, into receivers, whence it was again lifted to its proper tank. The exhausted ore was allowed to lie for another 12 to 15 hours in water and was then washed for 12 hours more. Fresh acid was diluted with a portion of the acid mother liquor. For each 100 parts by weight of copper, 550 to 700 parts of hydrochloric acid of 12° to 13° B. were employed. This form of lixiviation had to be abandoned because the carbonates of the ore were replaced by sulphides in depth.

At Twiste in Waldeck, attempts were made to leach the copper ores (malachite and azurite) occurring in the Bunter Sandstein (Lower Trias) and containing ¾ to 1 per cent. of copper, by means of hydrochloric acid, but had to be abandoned because the ores contained from ½ to 1 per cent. of lime, which was dissolved by the acid before it attacked the copper.

Lixiviation with Solutions containing Ferrous Chloride

Cupric oxide and cupric carbonate are decomposed by solution of ferrous chloride, forming cupric and cuprous chlorides and oxide of iron, and in the cases of carbonates, also free carbon dioxide, in accordance with the equations:—

$$3CuO + 2FeCl_2 = Fe_2O_3 + CuCl_2 + Cu_2Cl_2$$
$$3CuCO_3 + 2FeCl_2 = Fe_2O_3 + CuCl_2 + Cu_2Cl_2 + 3CO_2.$$

The oxide of iron is precipitated, whilst the chlorides of copper pass into solution, cuprous chloride, which is insoluble in water, dissolving in the excess of metallic chlorides.

[1] *Zeitsch. des Vereins deutscher Ing.*, 16, 305.

The action of ferrous chloride on copper carbonate was demonstrated by experiments of Schaffner and Unger[1] as early as 1862, whilst the employment of ferrous chloride as a solvent for copper oxide was suggested some years afterwards in America by Messrs. Sterry Hunt and James Douglas. The latter have founded their "Hunt and Douglas" process upon the above reaction, which process has been introduced in several places in the United States, but has undergone notable modification in recent years.

As only cupric oxide or carbonates are suitable for this process, cuprous oxide must first be converted into cupric oxide by ignition in the presence of air.

According to the original procedure, the solvent, namely ferrous chloride, was produced from common salt and green vitriol, which by double decomposition form ferrous chloride and sodic sulphate; 120 parts by weight of salt were dissolved in 1000 of water and 280 parts of green vitriol added; then another 200 parts of salt were added. After the solution was separated from the sodic sulphate, which crystallised out, it was ready for use. The ground ore was stirred in wooden tubs with the solution which was heated up to 70° C until the copper was extracted; the solution was then filtered to separate it from the residue and from the precipitated oxide of iron.

The filtrate was treated with iron, which both precipitated the copper and reproduced the original solvent. From cuprous chloride and iron, ferrous chloride and copper are formed, whilst, when both cupric and cuprous chlorides are present as in this case, ferric chloride is first formed, thus:—

$$2CuCl_2 + Cu_2Cl_2 + 2Fe = Fe_2Cl_6 + 4Cu.$$

Ferric chloride, however, and iron react, producing ferrous chloride:—

$$Fe_2Cl_6 + Fe = 3FeCl_2.$$

An action of atmospheric air upon the ferrous chloride solution, forming a precipitate of basic iron chloride (iron oxychloride) thus:—

$$6FeCl_2 + 3O = 2Fe_2Cl_6 + Fe_2O_3,$$

cannot be prevented, although it occasions the loss of some chlorine, as also of some copper which is mechanically retained as oxide or chloride by the precipitate. This loss of chlorine must be made good by the addition of fresh salt. Any silver that may be present is converted into chloride by the chloride of copper, and is dissolved in the excess of salt. The process was carried on successfully for some time

[1] *Berg.- und Hüttenm-Zeitung*, 1862, p. 173.

at Phœnixville, Pennsylvania, where cupriferous mattes containing about 20 per cent. of copper and 20 ounces of silver to the ton of copper, together with some oxidised local ores, were treated. The crushed mattes and ores mixed with 5 per cent. of salt were roasted sweet, and then leached in vats holding about 5 tons. The cement copper produced contained 75 to 80 per cent. of copper.

The advantage of the process lies in its requiring relatively small quantities of iron for the precipitation of the copper, as part of the latter is present in the cuprous state in which it needs only half as much iron to precipitate it as from a solution of cupric salt. The objections to it are the formation of basic salts, and the difficulty of separating the solution from the residue, on account of the precipitate of hydrated oxide of iron, which clogs the filters. The removal of silver is also injurious in the case of such ores as are to be treated for silver after the copper has been got rid of.

To avoid these objections, the Hunt and Douglas process has been altered as follows: the copper is dissolved out by dilute sulphuric acid, and ferrous or calcic choride is added to the solution, when cupric chloride is formed; if calcium chloride has been employed, a precipitate of calcium sulphate is thrown down, which must be separated from the solution. Sulphur dioxide is forced into the solution, by which the copper is precipitated as cuprous chloride:—

$$CuCl_2 + CuSO_4 + SO_2 + 2H_2O = Cu_2Cl_2 + 2H_2SO_4.$$

The cuprous chloride is separated from the solution, and treated with iron or milk of lime producing metallic copper or cuprous oxide and solution of ferrous chloride or calcic chloride. Into the filtrate from the cuprous chloride precipitate, hot air is blown by means of a Korting's injector, which expels any free sulphur dioxide that may be left in it. The solution which after this treatment consists mainly of sulphuric acid is again used as a solvent for copper, whilst the solution resulting from the precipitation of the copper by iron or lime, and which contains ferrous chloride or calcic chloride is used again for the chlorination of copper in the copper sulphate solution. The cuprous oxide produced by treating cuprous chloride with milk of lime is to be smelted with charcoal for metallic copper.

This method has the advantages that no ferric hydrate is formed as in the original Hunt and Douglas process, that silver is not dissolved by the dilute sulphuric acid, and that the precipitation of the copper, the whole of which is present in the cuprous state, requires a relatively very small quantity of iron. The precipitated copper is, moreover, said to be very pure. This process is not used for ores

but has been introduced at Kansas City, Missouri, for the extraction of copper from calcined argentiferous lead and copper mattes. No data as to the practical results are at present available.

At Deva in Siebenbürgen[1] a process with ferrous chloride as the solvent, but differing from the Hunt and Douglas process, has been used according to Hauch for ores containing malachite with 2 per cent. of copper. The ore was stamped fine, and charged in 12 cwt. lots upon the perforated false bottom of a vat, upon which it was spread out. So much cold ferrous chloride solution was then run in as to stand 8 inches above the top of the layer of ore. The ore was continually turned over whilst the solution was allowed to run off from the true bottom of the vats, and continually poured back again for a period of 3 hours. Then 26 lbs. hydrochloric acid of 20° B were added and allowed to act for 24 hours, with constant circulation, upon the ore, which was meanwhile repeatedly turned over. By this means the copper was dissolved out of the ores down to 0·12 per cent. The precipitation was performed by means of iron. This process is not however, free from the objections pointed out above.

At Rochlitz in the Riesengebirge fruitless attempts were made in the fifties of the present century to extract copper from sandstone containing azurite and malachite by means of ferrous chloride.

When copper ores containing lime are being treated, there is the difficulty to be contended with that ferrous chloride and calcic carbonate, in the presence of air, are decomposed into calcic chloride and ferric hydrate.

Lixiviation with other Solvents

Ammonic carbonate can be used on ores whose gangues are attacked by acids, for instance, calcareous ores containing carbonate of copper. In this case, however, no sulphates may be present, because they are decomposed by ammonic carbonate, producing ammonic sulphate and calcic carbonate. Experiments hitherto tried in this direction have failed because ammonia-tight vessels were not employed, and because the precipitation of the copper, for which iron cannot be employed, was performed by means of sulphuretted hydrogen, sulphide of calcium or sulphide of barium. By the use of iron vessels, however, loss of ammonia may be avoided; the copper can be obtained as oxide by distilling off the ammonia, which can thus be recovered. Hyposulphite of sodium has been proposed by Strohmeyer for the solution of copper carbonate, the copper to be precipitated by

[1] *Oesterr. Zeitsch.*, 1876, p. 489. *Berg.- und Hüttenm. Ztg*, 1877, p. 308.

means of sulphide of sodium. On account of the ready decomposibility of the solvent, and the retardation of solution in the presence of lime, this method has not come into use.

Ferric sulphate is not employed by itself, but only in combination with sulphuric acid. It is contained in the mother liquor after copper has been precipitated by iron from a solution of sulphate, which mother liquor is used, after green vitriol has been crystallised from it, together with fresh sulphuric acid as a leaching agent. It acts both in virtue of the free sulphuric acid and of the ferric sulphate which it contains. Ferrous sulphate, too, will dissolve cupric oxide with the separation of basic ferric sulphate.

The action of ferric sulphate is the following :—

$$Fe_2O_3,3SO_3 + CuO = CuSO_4 + Fe_2O_32SO_3.$$

b. Precipitation of the Copper. The copper may be in solution as sulphate, as cupric or as cuprous chloride. The precipitant that should generally be used for such solutions is metallic iron. It is also used for solid cuprous chloride, thrown down as previously explained.

Other precipitants, which may be exceptionally employed (where iron is not to be had or is very expensive) are sulphuretted hydrogen or aqueous solutions of sulphides, which precipitate copper as sulphide, as also milk of lime for cupric chloride solution, and for cuprous chloride in solution or solid. Milk of lime precipitates cupric hydrate from cupric chloride, and cuprous oxide from cuprous chloride; it also throws down copper as cupric hydrate from a solution of the sulphate but the precipitate is mixed with sulphate of lime, which is simultaneously formed. The precipitates of hydrate formed by milk of lime are very voluminous and troublesome to smelt. Up to now the precipitation of copper as sulphide (see page 209), as hydrate or as suboxide, has in no case come into regular use.

For the precipitation of copper by iron, it is desirable that the solution should contain as little free acid or ferric salts as possible, otherwise a large quantity of iron is dissolved without contributing to the precipitation of the copper. Theoretically, to precipitate 100 parts by weight of copper from cupric sulphate or chloride solution, 88·8 parts of iron are required, but from a solution of cuprous chloride or from the solid salt, only 44·4 parts. In practice, however, the consumption of iron is considerably greater, because the solutions cannot be kept free from acids and ferric salts. When these are present in large quantity, the consumption of iron may rise to 200 or 300 parts to 100 of copper, especially in the case of sulphate solutions con-

taining iron. The ferrous sulphate by prolonged contact with the air is decomposed into free sulphuric acid and ferric sulphate; the former dissolves iron, and the latter takes it up, forming ferrous sulphate.

Ferric chloride contained in hydrochloric acid solutions takes up iron forming ferrous chloride.

An especial disadvantage attending the formation of basic salts is that these render the precipitated copper or "cement copper" impure. It is therefore necessary to get rid as far as possible of acids and ferric salts before the precipitation, and to conduct the latter as rapidly as possible.

The best method of eliminating free acids or of preventing the formation of basic salts is to continue the action of the solutions on the ores till the former are completely neutral, and then at once to proceed to the precipitation of the copper. Further, the neutralisation of free acids by lime, the previous separation of basic iron salts by heating the solution, and the reduction of ferric to ferrous sulphate by sulphur dioxide have all been proposed, but have only found a very limited application.

Turbid solutions must be allowed to clear in special settling tanks before precipitation. If the solutions contain silver, the latter is first precipitated by copper, iodide of potassium, sulphuretted hydrogen, or by blowing iron dust into the solution.

Various proposals have also been made for the removal of arsenic and antimony (which bodies are also precipitated by iron) from the solution, but none of these have been found sufficiently perfect to be adopted. According to Down,[1] arsenic and antimony are only precipitated by iron from strongly acid, but not from feebly acid solutions. According to Kingzett and Lunge,[2] as also Gibb, they are on the other hand said to be precipitated completely, the precipitate having a composition similar to that of Scheele's Green.

Iron is used in the form of wrought iron, pig iron, iron sponge and iron bears. Pulverulent iron in the form of ground sponge acts most rapidly, then follow iron turnings and sheet iron (clippings from sheet mills and button makers). Bar iron yields a coarse-grained cement copper, with but little coherence; grey pig iron, which acts faster than white, gives a more pulverulent precipitate, whilst white iron throws down coherent masses. The graphite in the pig iron separates out during the precipitation and renders the cement copper impure.

Clippings of tin plate can also be used to precipitate copper; if

[1] *Dinglers' Journal*, 224, 195. [2] *Ibid.* 219, 330.

the latter is in solution as chloride, the tin can be separated as oxide.[1]

Precipitation of copper is facilitated by heating the solution, stirring it, and presenting the largest possible surface of iron, for which reason the latter is best in the form of powder.

The solution may be heated direct by allowing a flame to impinge upon the liquid or by leading steam into it, or indirectly by allowing the heated products of combustion or steam to circulate through pipes in the precipitating vats.

The liquor may be stirred by means of special apparatus in the vats or by revolving the closed vats, or by blowing air into the liquid, or by allowing the solution to run through a series of troughs placed stepwise, one below the other. The precipitating vessels are tanks, troughs or vats of wood, often lead-lined. The precipitation of copper is complete when the bright surface of a piece of iron dipped into the solution is no longer coated with a film of copper.

In Stadtberge the precipitation of copper from the hydrochloric acid solution takes place in a cylindrical vat about which clay is rammed. Inside it there is a second cylinder open at both ends, made of wooden slats, which is connected with the outer vat by means of a horizontal grid consisting of radially disposed wooden slats. In the inner cylinder is a vertical shaft carrying a wooden stirring vane. The iron used for precipitation is piled on the grid between the walls of the vat and the inner cylinder.

The shaft is driven by gearing, and the vane revolving drives the solution against the iron, thus washing down the copper deposited on the latter to the bottom of the vat, whence it is removed from time to time.

The arrangement of this effective contrivance is shown in Fig. 134. *G* is the inner lattice-work cylinder, *r* the horizontal grid, and *z* the bottom of the vat.



FIG. 134.

At Stadtberge 127 parts by weight of iron were required to precipitate 100 parts of copper from the solution of chlorides. In the old Hunt and Douglas process 60 to 70 parts of iron were consumed, and still less—about 50 parts—in the newer process. The greatest consumption is in precipitating copper from solutions of sulphates, when it amounts to 200 to 300 parts for each 100 of copper.

The products of precipitation with iron are cement copper and mother liquors. The former is a mixture of metallic copper with

[1] *Berg.- und Hütten-Ztg.*, 1877, p. 365.

basic salts of iron, particles of iron, graphite, and perhaps also silica, antimony, arsenic and ferric arseniate. It is washed as clean as possible from these impurities, and either smelted for coarse copper when it is impure, or else refined direct. (See treatment of cement copper, page 246.) The mother liquors contain chiefly sulphate or chloride of iron. The sulphates are in part used for the manufacture of green vitriol by evaporation and allowing the green vitriol to crystallise out, and in part used again as solvents. The chlorides are partly used again as solvents for copper.

2. THE EXTRACTION OF COPPER FROM ORES WHICH CONTAIN IT IN THE FORM OF SULPHATES

Copper existing as sulphate is dissolved in water and then precipitated by means of iron. Very often copper is found dissolved in mine waters (cement waters), and then only needs to be precipitated.

The lixiviation of the sulphate is performed in wooden vats or in tanks of wood or masonry, or else in loose heaps lying upon a floor of stamped clay or loam. Wooden tanks are either surrounded with clay or their joints are made tight with tarred hemp or red lead; masonry tanks are coated inside with asphalte or cement. Above the bottom of the leaching vessel there is a false bottom of slats or of perforated planks or acid-proof slabs of stone with open joints between them. Upon this false bottom a filter of straw, brushwood, heather or coke is arranged, and upon this the ore is dumped. Water is poured over it, which, in percolating through the ore, takes up the sulphate of copper and passes through the filter and the false bottom to the bottom of the tank. This bottom has a gentle slope, so that the liquid runs over it through an open gutter or through a wooden or leaden pipe. An indiarubber pipe that can be closed by clamps may also be employed.

Leaching tanks are best arranged on one level; the leaching is performed by causing the solutions to circulate, and as already pointed out, letting fresh water flow on to almost exhausted ore, and nearly saturated solution upon fresh ore. The process of Buff-Dunlop, for producing automatic circulation in the lixiviation of crude soda, cannot be applied here because the mass is not sufficiently porous. The solutions are best allowed to run into receiving tanks, whence by means of injectors, pumps, elevators, &c., they are lifted either direct on to the ore masses to be further leached, or into high-level tanks, whence they are distributed to the leaching tanks.

The copper is precipitated by iron in the manner already explained.

Sulphuretted hydrogen is but rarely used, and only in such places where iron cannot be readily obtained. It is best generated by leading sulphur dioxide and water vapour over red-hot coke or charcoal. For this purpose the gases produced in calcining sulphides in pyrites burners or kilns are aspirated by means of a Korting's injector, and forced together with the steam from the injector through a shaft furnace filled with glowing charcoal or coke. The sulphur dioxide is reduced to sulphur by the carbon, the water vapour forms with the red-hot carbon, hydrogen and carbon monoxide, and the hydrogen and sulphur combine to form sulphuretted hydrogen. The coke or charcoal are kept red hot by injecting a stream of air from time to time as in the production of water-gas.

A method devised by Sinding depends upon the action of sulphur vapour on hydrocarbons and hydrogen, another on the decomposition of sulphide of sodium by carbon dioxide.

Sinding generates producer-gas with raw fuel, and leads it over red-hot pyrites; by the action of the hydrocarbons and the hydrogen contained in the producer-gas upon the sulphur evolved from the pyrites, sulphuretted hydrogen is formed, and is made to traverse a chamber in which the cupriferous solution is dropping down in the form of fine rain. Gill and Gelstharp in England have produced sulphuretted hydrogen by the action of carbon dioxide on sodium sulphide.

More recently the method of Chance has been used, which consists in the treatment of residues from the Leblanc soda manufacture with carbon dioxide.

Precipitated sulphide of copper (CuS) is separated from the solution in filter-presses and is either roasted by the English reverberatory method or is converted by a blast of hot air into copper oxide and then smelted for coarse copper or refined copper.

As far as the author knows, this method of precipitation has been abandoned at Foldal (Norway) and Rio Tinto (Spain), where it was formerly in use. It was used in England at Swansea and at the Bede metal works.

As already stated milk of lime is not suitable for precipitating sulphate solutions.

Mine waters containing sulphate of copper, known as cement waters, are run through one or more systems of troughs, inclined at an angle of about 10°, arranged stepwise one beneath the other, filled with iron. The water escapes free from copper from the bottom trough.

At Schmöllnitz, Hungary, copper is obtained from mine waters. Iron rods are there arranged in gratings in the troughs; to precipitate the last portions of copper, after the solution leaves the last trough, it runs through vertical boxes in which it falls upon iron. The precipitation is promoted by the impact of the solution upon the iron. Cement copper with more than 55 per cent. of copper is refined, whilst with less percentage it is added to the charge of calcined matte, which is smelted for black copper in shaft furnaces. The most impure cement copper, with under 15 per cent. copper, is added to calcined copper pyrites to be smelted for matte. (Additional information on the extraction of copper from sulphate solutions will be found on page 240).

3. THE EXTRACTION OF COPPER FROM ORES THAT CONTAIN IT AS SULPHIDE

As already pointed out, copper that exists as sulphide must first be brought into a condition in which it can be treated with cheap solvents.

We have accordingly to distinguish:

(*a*) Transforming the copper into a form suitable for solution.
(*b*) Dissolving out the copper from ores and furnace products.
(*c*) Precipitating the copper from its solution.
(*d*) Converting the cupriferous precipitate into merchantable copper.

a. TRANSFORMATION OF THE COPPER INTO A FORM SUITABLE FOR SOLUTION

The sulphide of copper may be converted into sulphate, oxide or chloride, in order to render it readily soluble. The sulphate may be dissolved in water, the oxide in hydrochloric and sulphuric acids and in metallic chlorides, cupric chloride in water, and cuprous chloride in hydrochloric acid and solutions of metallic chlorides.

The Transformation of Sulphide of Copper into Sulphate.

This can be brought about by:—

1. Weathering of the ore.
2. Slow calcination.
3. Calcination with sulphate of iron or other easily decomposable sulphates.
4. Heating the ore with nitrate of iron.
5. Treating the ore with solution of ferric sulphate.

Weathering the Ore

This method can only be employed without previous calcination in the case of such ores as are specially prone to rapid decomposition, as is the case with cupriferous marcasite. Such ores are collected in heaps upon a floor of clay, and are left exposed for a considerable period to the action of the weather. Sulphates of copper and of iron are leached out. By repeated leaching and by pouring over them the acid mother liquors containing ferric sulphate, which are left when the copper is precipitated from the liquors, decomposition is promoted, because these liquors decompose sulphide of copper as follows:—

$$x\,H_2SO_4 + Cu_2S + 2Fe_2(SO_4)_3 = 2\,Cu\,SO_4 + 4\,FeSO_4 + S + x\,H_2SO_4.$$

It is, however, very difficult, in most cases even impossible, to convert the whole of the copper into sulphate within any reasonable time. Generally a considerable number of years is required to obtain even a moderate proportion of the copper in the form of sulphate.

Although this method of forming sulphate is cheap, it is only used exceptionally, because the capital invested in the ore lies unproductive for too long, and because the extraction of copper is imperfect. But, as before said, sulphate of copper that has been formed in the mine and dissolved in mine waters is utilised as a source of copper. Weathering is also employed as an auxiliary in the calcining process.

The Production of Sulphate of Copper by slow Calcination

The production of sulphate by slow calcination can only be used for ores that contain proportionately large amounts of iron pyrites and small amounts of copper pyrites. Unless sulphates are added, an even tolerably satisfactory proportion of sulphate of copper can only be produced by calcining in heaps or stalls. By the relatively rapid methods of calcining in furnaces, too large a proportion of oxide of copper is formed as compared with sulphate. But even slow calcination in heaps or stalls will not convert all the sulphide of copper into sulphate; a part always remains unaffected, whilst another part is transformed into oxides. In order to extract as much copper as possible from the ores, after the calcination has been finished and the sulphate of copper thus formed has been leached out, the ores are allowed to weather, whereby in the course of time the copper is converted into sulphate; or, provided there is sufficient copper in the ore, the calcination is so conducted that the sulphide of copper shall be concentrated in a kernel, whilst the sulphate remains in the

porous crust consisting chiefly of oxide of iron. The kernels obtained by this kernel-roasting are worked up in the dry way, whilst the sulphate of copper is leached out of the crusts.

The production of sulphate by calcination, without the formation of kernels, followed by weathering of the leached calcined ore, is used at Rio Tinto, in the province of Huelva, in Spain. The ores thus treated are cupriferous pyrites with 1½ to 2 per cent. of copper; these are slowly calcined in heaps of 200 to 1,500 tons upon a bed of brushwood, firewood, or coals. The 200 ton heaps are hemispherical, 26 feet in diameter at the base and 11 feet 6 inches high. The larger, 1,500 ton heaps are elliptical in plan, the longer axis of the ellipse being 55 feet 9 inches, and the shorter axis 32 feet 10 inches; their height is also 11 feet 6 inches. Air is admitted by means of a system of channels traversing the heaps. The smaller heaps burn for 2 months, the larger ones for 6. To calcine 100 tons of ore requires in the small heaps 27 cubic feet of wood and in the larger ones 9 cubic feet. The yield of copper is greater in the small heaps than in the large ones. The calcined ores are leached for 50 hours in the manner described on page 208, by which means the copper present as sulphate is washed out from them. The exhausted residues still contain 0·4 to 0·5 per cent. of copper, chiefly as sulphide, to extract which the ores are allowed to weather. With this object they are so piled on a system of horizontal flues built of dry stone, and connected with vertical flues 8 inches in diameter, also built of dry stone, that air can circulate through the pile of ore, The vertical flues are continued in proportion as the heap gets higher by the piling on of additional ore. As soon as the damp heap has reached a certain height, the sulphides begin to decompose, as is shown by the temperature rising. By checking the air supply it is kept, if possible, from rising so high that the heap takes fire. From time to time, the heap, or a portion of it, if it is a large one, is leached out, and the liquor conducted to the precipitating vessels. The exhaustion of the heaps, which are continually being increased and may reach 500,000 tons, will not be completed in measurable time, as, in spite of frequent leaching, the weathering proceeds very slowly. It is even held that these huge heaps will still be producing sulphate of copper long after the mines shall have been worked out.

At the foot of the large heaps, smaller piles of raw ore are also constructed, which, when they are thoroughly alight, are covered with calcined and raw ores. They are moistened to promote leaching as far as possible.

With the object of simplifying the complete conversion of the copper into sulphate, it has been proposed to do away with the method of leaching in special vats to be presently described, and to calcine the ore in smaller heaps on the above described system of flues; then to spread out the roasted ores, to build a second heap on this layer, to calcine that, spread it out in turn, and so on. The layers of ore, thus spread out, are leached from time to time. It is, however, to be feared that leaching in heaps would be neither as rapid nor as effective as leaching in vats, and that the complete extraction of the copper might therefore be still further delayed.[1]

The production of sulphate with the simultaneous production of kernels, or kernel-roasting, is only applicable to ores free from gangue and which do not decrepitate. It has been fully described on page 34. It was used at Agordo (Venice), Foldal (Norway), Kedabeg (Caucasus), and Wicklow (Ireland), but has been given up for reasons already enumerated.

The Production of Sulphate of Copper by Calcining Ores with Sulphate of Iron or Other Readily Decomposable Sulphates

By calcining finely ground pyritic chalcopyrite poor in copper, intimately mixed with sulphate of iron, it is possible to convert the greater part of the copper into sulphate. Sulphate of alumina acts like sulphate of iron, and according to Monnier an addition of sulphate of soda also promotes the formation of sulphate of copper.

The formation of sulphate by the aid of green vitriol or of the mother liquors, resulting from the precipitation of copper from solutions of its sulphate by means of iron, is best carried out by means of heap-roasting. Reverberatory furnaces are seldom used, because the quantity of sulphate formed is less on account of the more rapid calcination. Reverberatory furnaces have been used to obtain sulphate of copper from copper matte with the addition of sulphate of soda, or from copper speiss with the addition of iron pyrites, but they have only been employed quite exceptionally for the direct production of sulphate of copper from ores. Reverberatory furnaces were, however, used in conjunction with stalls at Balan in Siebenbürgen.

Simple heap roasting has been used with good results at Agordo in the Venetian Alps and at Majdanpec in Servia. At Agordo, the mine fines (iron pyrites with 1 to 2 per cent. of copper) were crushed fine, made into a stiff paste with mother liquors containing sulphate of iron produced in precipitating the copper, and which had a density

[1] Knab, *Traité de Métullurgie*, p. 146.

of 26° to 30° B., and then pressed in brass moulds into truncated conical lumps 3 inches high and 4 inches across at the base. These lumps were air-dried for 3 weeks, and then built into heaps. The heaps were covered with mine smalls, over which was a covering of exhausted crusts from kernel roasting. When dry crusts were available they were used to cover small heaps without the layer of mine smalls. If the latter were replaced by damp crusts, the upper layers of lumps were found to absorb moisture from them and to become agglomerated, when the conversion into sulphate was unsatisfactory. For small heaps the calcination lasted from 4 to 5 months, for large ones from 10 to 12. The greater part of the copper was thus converted into sulphate, being aided by the decomposition of the sulphate of iron, which splits at high temperatures into sulphur trioxide and oxide of iron.

At Majdanpec in Servia,[1] ores containing under 2 per cent. of copper, partly as chalcocite, and partly as malachite and cuprite, were mixed in the proportion of 12·5 parts by weight of oxidised and 9·5 of pyritic ores, after being crushed, and made into bricks of 11 lbs. weight. As shown by the subjoined analysis, the ore mixture contained so much moisture and sulphates that no artificial additions were required:—

Cu_2S	1·05
$CuCO_3$	0·30
Cu_2O	0·95
Fe_2O_3	9·51
FeS_2	34·39
H_2SO_4	1·02
$CaCO_3$	5·74
SiO_2	12·32
$MgSO_4$	4·56
$Al_2(SO_4)_3$	3·51
Al_2O_3	3·81
H_2O	16·00
As, Ag	traces.

The ores were piled in heaps, dried for a month, and then calcined in heaps of 300 tons with a consumption of 7 tons of beech faggots, the heaps being covered with a layer of mine smalls. The calcination lasted 3 months, during which the various copper compounds were converted into sulphate by the sulphur trioxide produced by

[1] *Berg.- und Hütten.-Zeitung*, 1885, p. 58.

the decomposition of the sulphates of iron and alumina as well as by the calcination of pyrites. In the interior of the heap the copper was converted into sulphate down to $\frac{1}{8}$ to $\frac{1}{4}$ per cent., in the outer parts down to $\frac{1}{2}$ to $\frac{3}{4}$ per cent.

At Balan in Siebenbürgen, Transylvania, calcination in reverberatory furnaces is combined with stall roasting, according to Flechner.[1] The ores contain 1·5 to 2·3 per cent. of copper, some pyrites and 78 to 84 per cent. of gangue; the latter consists of 52 to 54 per cent. of silica, 20 to 22 per cent. of ferrous oxide, and 5 to 8 per cent. of alumina. The ores are first roasted in quantities of 30 to 40 tons in stalls, whereby $\frac{1}{4}$ of the sulphur is removed, then crushed, made into a paste with ferrous sulphate mother liquor of 4° to 6° B, stacked in heaps of 15 to 20 tons, and left for some days, after which, they are calcined in reverberatory furnaces fired by gas. The copper is said to be converted into sulphate and leached out, down to 0·4 to 0·7 per cent. The leaching is performed with mother liquors, resulting from the precipitation of the copper. The exhausted ores are allowed to weather, to be again subsequently leached. The formation of sulphate is said to reach its maximum when the ores contain 25 per cent. of sulphides.

Formation of Sulphate of Copper by Heating the Ores with Nitrate of Iron

Perrino proposes to heat copper pyrites with nitrate of iron to a temperature of 50° to 150° C; this process is said to transform the copper into sulphate, whilst sulphide of iron is not attacked. The nitrous fumes evolved are to be oxidised by the air to nitric acid again, which is to be used to regenerate nitrate of iron. This process which dispenses with calcination, has not yet been employed on the large scale.[2]

Formation of Sulphate of Copper by the aid of Ferric Sulphate.

As already stated, sulphide of copper is converted into sulphate by the action of ferric sulphate in accordance with the equation:—

$$x\mathrm{H_2SO_4} + \mathrm{Cu_2S} + 2\mathrm{Fe_2(SO_4)_3} = 2\mathrm{CuSO_4} + 4\mathrm{FeSO_4} + \mathrm{S} + x\mathrm{H_2SO_4}$$

This process acts as a subsidiary process during the leaching of ores roasted for sulphate or weathered, in that the liquors always contain large quantities of ferric sulphate, which promote the formation of sulphate from sulphide and oxide of copper.

[1] *Oesterreich. Zeitschrift*, 1882, p. 355; 1883, pp. 455, 463.
[2] *Berg.- und Hüttenm.-Zeitung*, 1888, No. 20.

Ferric sulphate has not been used independently for wet methods on account of its comparatively slow action, but has been proposed for decomposing sulphide of copper for an electrolytic method. (See page 249.)

THE TRANSFORMATION OF SULPHIDE OF COPPER INTO OXIDE

This is effected when the calcined ore is to be treated by the already-described Hunt and Douglas process. It may also be used when sulphuric or hydrochloric acids are to be obtained very cheaply. For economic reasons it is, however, preferred to convert sulphide of copper into chloride by calcination with salt, or to calcine for sulphate rather than to convert the sulphide into oxide of copper. Apart, therefore, from the Hunt and Douglas process, the conversion of sulphide into oxide of copper is only undertaken under exceptional circumstances. In the case of furnace products, *i.e.*, argentiferous copper mattes, sulphide of copper is more often converted into oxide with a view to dissolving the latter in sulphuric acid (*i.e.*, at Freiberg) Argentiferous mattes are also prepared in the same way for treatment by the new Hunt and Douglas process.

Sulphide of copper is converted into oxide by calcination of the crushed ores in reverberatory furnaces, or in muffle furnaces if sulphuric acid is also to be made. These furnaces are similar to those described under the dry methods of copper extraction. By the calcination of ores in heaps, stalls and shaft furnaces, the object is only imperfectly attained, as not all the sulphide of copper is converted into oxide.

As an example of the oxidising calcination of ores for the production of copper oxide, Ore Knob in the United States may be cited, where iron pyrites containing chalcopyrite is calcined in reverberatory furnaces with three hearths. The ore, which is rabbled every ¾ hour remains 12 hours on each hearth. The calcined ores contain 7·75 per cent. of oxide of copper and 4·15 per cent. of sulphate.

THE CONVERSION OF SULPHIDE OF COPPER INTO CHLORIDE (CUPROUS OR CUPRIC)

This operation may be performed in the wet or in the dry way, in the wet way by treating the ores with ferric chloride or with ferrous chloride and hydrochloric acid, in the dry way by calcining with salt. The wet method is slow, whilst dry chlorination is rapid and relatively thorough. The dry way should therefore be employed as a rule, and the wet way only used when the cost of dry chlorination becomes

excessive on account of the high price of fuel, or when on no consideration can the products of calcination be allowed to escape into the atmosphere, however completely the hydrochloric acid may first have been condensed.

Formation of Chloride of Copper in the Wet Way

The conversion of sulphide into chloride of copper by means of ferric chloride is applied at Rio Tinto to cupriferous pyrites with an average of 2·68 per cent. of copper; it is there known as the "Dötsch" process, after the name of its inventor. Sulphide of copper is converted into cuprous or cupric chloride in accordance with the following equations:—

$$CuS + Fe_2Cl_6 = 2FeCl_2 + CuCl_2 + S$$
$$Cu_2S + Fe_2Cl_6 = 2FeCl_2 + Cu_2Cl_2 + S.$$

The result is a solution containing cupric chloride, cuprous chloride dissolved in ferrous chloride, and ferrous chloride. After precipitation of the copper by iron, ferric chloride is regenerated by leading chlorine into the solution.

The ore is broken by rock-breakers into pieces of 0·06 cubic inch and stacked in heaps 49 ft. 3 inches square, and 13 feet high, in which there are a series of dry stone horizontal and vertical flues, just as there are in the heaps for producing sulphate of copper at Rio Tinto. When the heaps are built up, a mixture of ferric sulphate and salt is distributed through them in such proportions that the two substances may interact forming ferric chloride and sodic sulphate. Ferric sulphate is obtained at Rio Tinto as a decomposition product of iron pyrites and of solutions of ferrous sulphate. The heaps are then moistened with liquors containing ferric chloride when the above reactions take place. To ensure as uniform a distribution as possible of the fluids, wooden tanks, 32 feet 9 inches square, are erected on the heaps, into which the liquors are pumped by rubber pumps. The solutions percolate through the heaps and run off at their foot into the precipitating vessels, in which the copper is precipitated by iron. After the ferrous chloride of the resulting liquor has been transformed into ferric chloride by means of chlorine, the liquor is again pumped up and used over again. The liquors flowing from the heaps contain 11 to 15½ lbs. of copper in 35 cubic feet of solution. By this means one half of the copper in the ore (1·34 per cent. of the ore) is transformed into chloride and dissolved out within 4 months. Of the remaining copper 0·86 per cent. is extracted in 2 years more. The residues contain 0·48 per cent. of copper, which is lost.

The ferrous chloride in the liquor is retransformed into ferric chloride by letting it fall in a fine shower through a tower filled with pieces of wood, quartz or coke, in which gases containing chlorine are made to ascend.

The chlorine is obtained by heating salt with sulphate of iron in a reverberatory furnace, the iron being half in the ferrous and half in the ferric state; in the reverberatory furnace it is all converted into ferric sulphate. The charge is 4 cwt.; air enters the furnace through three working doors and through a hollow fire bridge.

The reactions that ensue are the following :—

$$2FeSO_4 + 4NaCl + 3O = Fe_2O_3 + 2Na_2SO_4 + 4Cl$$
$$Fe_2SO_6 + 2NaCl + O = Fe_2O_3 + Na_2SO_4 + 2Cl.$$

Together with these reactions, others producing a certain amount of hydrochloric acid also take place; in order to convert this as far as possible into chlorine, a certain quantity of oxide of manganese is piled on the furnace bed, close to the fluebridge. The gases evolved are led into the above mentioned towers, in which the chlorine contained in them regenerates the ferric chloride.

Attempts have been made at Rio Tinto to shorten the chlorination by first digesting the ores with ferric chloride in vessels and afterwards stacking them in heaps and treating as above described. By digestion with ferric chloride it was found possible to chloridise $\frac{1}{8}$ to $\frac{1}{5}$ of the copper present and to get it into solution within 10 days. By this plan in conjunction with chloridising in heaps it is hoped that the total process may be finished in less time than by chloridising in heaps alone.

The sulphur of the iron pyrites is but little attacked in the Dötsch process so that the leached ore can still be used for the manufacture of sulphuric acid. As this process entirely avoids calcination, it is worth considering in localities where sulphuric acid is not manufactured, and where at the same time sulphurous fumes may not be allowed to escape into the atmosphere.

The transformation of sulphide into chloride of copper by means of ferrous chloride and hydrochloric acid is performed at Stadtberge in Westphalia.

This process depends on the fact that ferrous chloride containing hydrochloric acid, when exposod to the air, is partly converted into ferric chloride and ferric hydrate, the latter being also converted into ferric chloride by the hydrochloric acid. Ferric chloride chloridises the sulphide of copper as above explained, with the formation

of ferrous chloride. The chloride of copper is dissolved out of the ore by means of liquors rendered acid with hydrochloric acid, and the copper is precipitated by iron from the solution of copper chloride and ferrous chloride, which is thus obtained. The mother liquor is employed, in part mixed with hydrochloric acid for chloridising fresh ore, and in part for dissolving out the chloride of copper when formed.

Chloridation takes place when the ore, saturated with the solution of ferrous chloride and hydrochloric acid is stacked in heaps and allowed to weather.

The ore at Stadtberge is a siliceous schist containing 2 to 2 ½ per cent. of copper chiefly in the form of chalcocite, partly as sulphate (⅓), and to a smaller extent in an oxidised state. An average analysis gave the following result:—

SiO_2	74·28	
Al_2O_3	10·88	
Fe	2·17	
Cu	2·328	(of which 1·03 per cent. in soluble in HCl.)
Ag	0·0025	
CaO	0·61	
P_2O_5	0·48	
S	1·53	
SO_3	0·155	
CO_2	0·710	
H_2O	0·585	
Loss on ignition	6·510	

The ores are broken down in rockbreakers and then crushed between rolls to 0·09 to 0·12 cubic inch; they are then transferred to wooden tanks round which clay has been rammed, provided with wooden false bottoms about 6 inches above the actual bottom. Each tank holds 100 tons which forms a layer 35 to 40 inches deep on the false bottom. The chloridising solution is lifted by means of a bucket wheel and poured over the ore which it completely covers. It is allowed to act for three days and is rendered more energetic in its action by being run off from time to time and then poured on again. The solution consists of the mother liquor resulting from the precipitation of the copper by iron and contains per gallon:—

Ferrous chloride	1·7797 lbs.
Ferric chloride	0·0264 „
Cupric chloride	0·0112 „
Sodic chloride	0·0133 „
Aluminic chloride	0·0977 „
Calcic sulphate	0·0788 „

For each cwt. of ore, 4½ lbs. of hydrochloric acid of 20° B are added. In order to dissolve the minute quantity of silver contained in the ore, which is converted into chloride by the solution, 2 lbs. of salt are added for each gallon of liquor. Sulphate and oxide or carbonate of copper are dissolved by the solution, thus rendering the ore more porous and better adapted for the weathering that follows the saturation. After this action has gone on for three days the copper in the ore is reduced to between 1·2 and 1·5 per cent.; the liquor is then run off and is used for dissolving the chloride of copper from the weathered ore.

The ores saturated with the chloridising solutions are removed from the tank, stacked in heaps 10 feet high, and exposed to the weather for three months, during which time they become dry. At the end of this time the greater part of the copper (all except 0·4 per cent.) has been converted into cuprous and cupric chlorides, oxychloride and sulphate of copper, and the silver into chloride of silver. The ores are now leached with liquors containing hydrochloric acid, which are in part the solutions that have been used for saturating the ore, till only 0·4 per cent. of copper remains, and are allowed then to weather still further upon a bed of clay, when some more copper is obtained.

The process gives a good yield of copper and entails a comparatively small consumption of iron for precipitation, namely, 105 parts iron to 100 parts of copper.

Production of Chloride of Copper in the Dry Way

This method is largely used at present in Europe, for extracting copper from cupriferous pyrites containing only a moderate quantity of copper (3 per cent. to 8 per cent.). It consists in an oxidising calcination of the ores, performed in shaft furnaces if the sulphur vapours are to be utilised for sulphuric acid making, and a subsequent chloridising roasting with salt or *Abraumsalz* in reverberatory or muffle furnaces, whereby the copper is converted chiefly into cupric and only in small part into cuprous chloride. The chloride of copper is leached out and the copper precipitated from the solution by means of iron.

The method had long previously been proposed by Longmaid Schaffner, Becchi and Haupt, but was only introduced in England in consequence of the experiments, on a large scale, of Henderson, Phillips, Tennant and others, when it was employed upon the cupriferous pyrites of Spain and Portugal. It was afterwards adopted in Germany, Austria, Belgium and Sweden. It is in use at present in

England (Tyne district and South Lancashire), Belgium (Hemixem near Antwerp), Sweden (Atvidaberg and Fahlun), Germany (Duisberg, Königshütte, and till recently at Oker), and Austria (Aussig in Bohemia and Wittkowitz near Mährisch-Ostrau). It is especially important for Spanish, Portuguese, Norwegian and Hungarian pyrites with an average copper contents of 3 to 4 per cent.; these ores are first calcined in sulphuric acid works down to 3 or 4 per cent. of sulphur and then disposed of to copper or iron-works. The copper is extracted by means of this process and the residues, consisting chiefly of ferric oxide, are used in iron works as a source of iron.

The English process has been described by the following writers: Clapham (Chem. News, xxiii. 26; Wagner's Jahresberichte, f. 1871, 134); Wedding and Ulrich (Preuss. Minist. Zeitschr, xix. 298.); Lunge (Dingl. Journ. cciv. 288; cxiv. 466; ccxv. 54 and 229; ccxix. 323; Wagner's Jahresberichte, f. 1872, 170; 1875, 188 and 307; 1876, 175; Handbuch der Soda-Industrie, Brunswick, 1879, Vol. I p. 544), Gibb (Chem. News, xxxi, 165). Braüning has communicated an article on the process at Oker to the Preuss. Minist. Zeitschr. 1877, p. 156.

The process depends upon the reaction which ensues when calcined pyrites, which still contains some 4 per cent of sulphur mainly in the form of sulphide of iron, is roasted with sodium chloride or with the so-called *Abraumsalz* (chlorides of sodium, magnesium, potassium and calcium); sulphate of copper is formed, which forms by double decomposition cupric or cuprous chloride and sodic sulphate. The formation of cupric sulphate is due chiefly to the sulphuric acid of the sulphate of iron which partly exists ready formed in the calcined ore, and partly is produced from the sulphide of iron, and which in part is split up into ferric oxide and sulphur trioxide and in part forms with the sodic chloride sodic sulphate and ferrous and ferric chlorides, which latter substances exert a chloridising action upon the copper. A part of the sulphuric acid resulting from the decomposition of the sulphate of iron evolves chlorine from the salt if it is anhydrous, and hydrochloric acid if it is in the hydrated state. Chlorine chloridises sulphide of copper, and hydrochloric acid the metallic oxides present.

The result of the calcination is a mixture of cupric chloride, oxide and sulphate, cuprous chloride, sodic sulphate, ferrous chloride, ferric oxide, and sulphates and chlorides of the remaining metals contained in the ore. The calcination must be so conducted as to produce the minimum possible of copper compounds insoluble in water, namely copper oxide and cuprous chloride, because these bodies require acids

or chlorine compounds to dissolve them. Soluble ferric sulphate too should not remain in the calcined ore, because it passes into the solutions and entails an increased consumption of iron when the copper is precipitated.

The necessary conditions for success are: not too high a proportion of copper in the ores, not too much sulphur and the maintenance of a suitable temperature during calcination.

If there is too much copper, the whole of the sulphide is not decomposed by the first calcination, so that part of the copper is not chloridised in the second roasting which is not hot enough to completely decompose sulphide of copper, and accordingly escapes solution. In Oker 8 per cent. was looked upon as the maximum for good chlorination, in England 6 per cent.

The sulphur must not exceed 1½ times the equivalent of the copper present, because otherwise too much salt would be consumed and the calcination would take too long. If the quantity of sulphur is insufficient, the necessary quantity of raw pyrites is added.

The temperature must not exceed low redness, otherwise too much cupric chloride would be volatilised; in spite of all precautions it is impossible quite to prevent the production of cuprous chloride and cupric oxide or the volatilisation of small quantities of cupric chloride.

The gases evolved in the chloridising roasting contain sulphur dioxide, hydrochloric acid and chlorine, and must therefore be rendered innocuous before being allowed to escape; this is effected by leading them into towers filled with acid proof stones or in the case of muffle furnaces with coke, down which water is allowed to trickle. The latter absorbs both the injurious gases and the volatilised cupric chloride. The towers are best built of masonry constructed of sandstone slabs soaked in tar, and their upper part is connected by stoneware or leaden pipes with stacks producing a strong draught.

The furnaces in which the calcination with salt (or *abraumsalz*) is effected, are either reverberatory or muffle furnaces; the former consume less fuel than the latter, but evolve the acid vapours that have to be condensed, in a highly dilute condition. They have fixed or partly movable bodies and are fired by ordinary grates or by gas. The calcining furnaces take a charge of 2 to 3 tons, which forms a layer 5 to 6 inches deep, and requires 8 to 12 hours for its calcination.

A reverberatory furnace with fixed body and fired by a grate, such as is used at the works of the Bede Metal Company at Hebburn-on-Tyne, is shown in Figs. 135 to 138. These furnaces are characterised



FIG. 135.

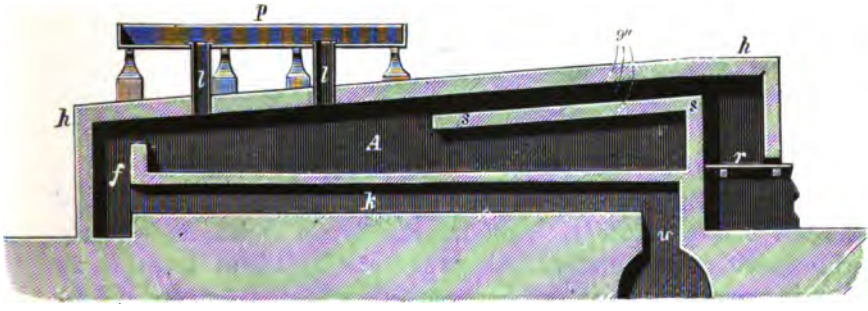


FIG. 136.

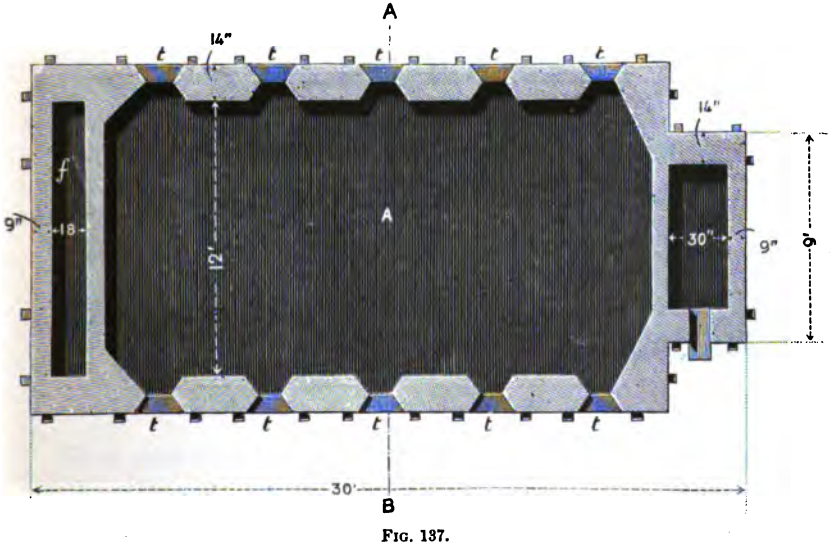


FIG. 137.

by a protecting arch, or curtain arch which reaches from the fire bridge almost to the centre of the furnace the object of which is to prevent the ore that lies near the bridge from being too strongly heated. The grate is shown at r; the flame from it passes through the space between the curtain arch s and the main arch h into the working body of the furnace A. At the end of the latter the gases enter the descending flue, f, and from this traverse eight flues, k, that

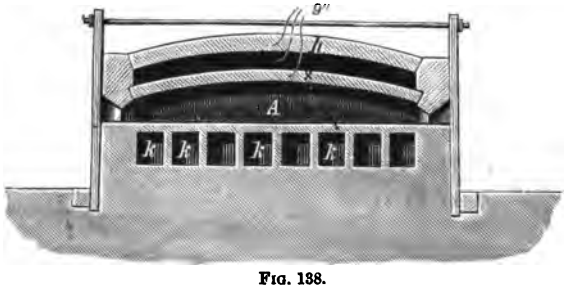


FIG. 138.

extend below the bed of the furnace. After they have thus heated the bed they pass into the subterranean flue, u, which leads to the acid-condenser. The working doors are at t, t; p is an iron pan for warming the charge previous to its entering the furnace, and l, l are boxes through which the mixture of ore and salt is charged. The furnaces hold 2 tons 16 cwt., and the time of calcination is 8 hours.

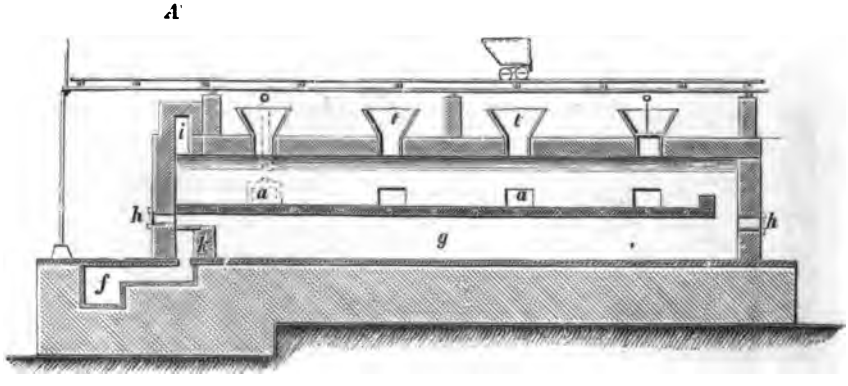


FIG. 139.

Figs 139 and 140 show a furnace with fixed body and fired by gas, such as are in use at Widnes in Lancashire, and were in use at Oker, where they were later on replaced by furnaces with ordinary

grates. (At present the wet method has been abandoned at Oker because the supply of poor ores suitable for it has fallen off).

From a producer not visible in the engravings, the gas enters a flue *k* running the entire breadth of the furnace, and thence five flues *g* running under the bed. Here it is burnt by means of atmospheric air which enters through apertures *h* that can be closed by slides. The flame passes first along the flues *g* under the bottom of the bed, and thence enters the body of the furnace. Thence the gases evolved pass through the flue *i* into a flue leading to the coke towers and thence to the stack.

The furnaces have 4 working doors *a* in each of the long sides and

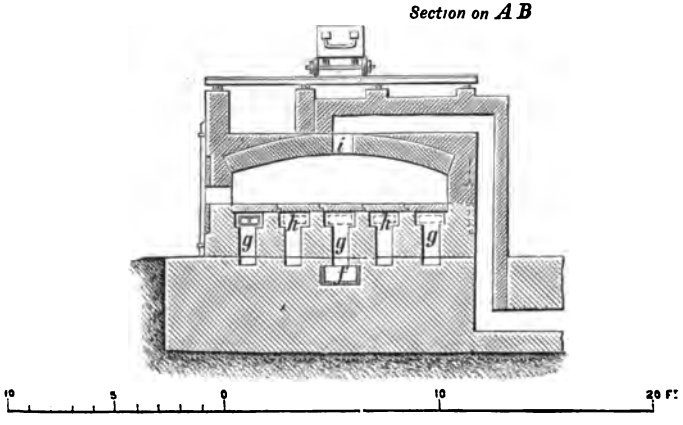


FIG. 140.

4 charging hoppers *t*. The charge is 2½ tons, and 2 charges are worked off in 24 hours.

The ores that used to be treated by the wet method at Oker had the following composition[1]:—

Pyrites	60 per cent.
Chalcocite	23 „ „
Zinc blende	6 „ „
Galena	2 „ „
Gangue	9 „ „

They were first calcined in pyrites burners, which delivered the fumes to the sulphuric acid works. The calcined ores contained from 6 to 9 per cent. of copper and 5 to 8 per cent. of sulphur; their

[1] Braüning, *loc. cit.*

chemical composition from the average of a month's working, was as follows:—

Copper (chiefly as oxide)	7·83 per cent.
Iron (chiefly as ferric oxide)	40·53 „ „
Lead (as oxide)	2·09 „ „
Silver	0·008 „ „
Zinc (chiefly as oxide)	1·95 „ „
Manganese (as sesquioxide)	0·40 „ „
Sulphur	3·80 „ „
Sulphuric acid	9·51 „ „
Alumina	4·43 „ „
Other gangue	11·65 „ „

Upon the assumption that the sulphur is mainly combined with iron, and the sulphuric acid with the metallic oxides (CuO, ZnO, CaO, FeO, Fe_2O_3), the proximate composition of the calcined ores would be somewhat as follows:—

CuO	9·80 per cent.
Fe_2O_3	53·14 „ „
FeS_2	7·13 „ „
PbO	2·25 „ „
Ag	0·008 „ „
ZnO	2·43 „ „
Mn_2O_3	0·57 „ „
SO_3	9·51 „ „
Al_2O_3	4·43 „ „
Other gangue	11·65 „ „
	100·918

The calcined ore was mixed with 15 per cent. of *abraumsalz* from Stassfurt and ground under edge-rollers to a mesh of 0·08 inch. The daily output of an edge-mill was 15 tons of ore with the corresponding amount of salt; $2\frac{1}{2}$ tons of the mixture was the charge for the gas-fired furnace, and this was heated to low redness within 4 hours. The mass was then rabbled for 5 hours with a very low fire or without any, the air valves being meanwhile kept open in order to allow the air to act upon the charge. The latter was then drawn and a fresh charge introduced as soon as the furnace was empty; 5 tons of calcined ore were worked off in 24 hours, with a coal consumption of 10 to 12 per cent. The composition of the ores after the chloridising roast (with 20 per cent. of the *abraumsalz*)

was as follows, according to determinatious made in the works laboratory at Oker :—

$CuCl_2$	8·17	soluble in water
$AgCl$	0·006	
$FeCl_2$	1·38	
$ZnCl_2$	3·42	
$MnCl_2$	1·71	
$NiCl_2$	0·15	
$CaCl_2$	3·17	
$Al_2(SO_4)_3$	0·56	
$MgSO_4$, $CuSO_4$, Na_2SO_4	20·50	
CuO	3·18	insoluble in water
Cu_2S	0·03	
$PbSO_4$	1·26	
Fe_2O_3	47·91	
Fe_2SO_6	1·02	
FeS_2	1·18	
Al_2O_3	0·44	
ZnO	0·46	
$CuSO_4$	1·19	
Insoluble	3·19	(insoluble in acids)

The average result obtained was that, of the total copper in the ores, after the chloridising roasting, 75 per cent. was soluble in water (cupric chloride and neutral sulphate), 20 per cent. in dilute acids (cuprous chloride, cupric oxychloride, oxide and basic sulphate) and 5 per cent. in aqua regia (cuprous sulphide).

The works at Oker were arranged in terraces for the sake of convenient transport of the solids and liquids. The arrangement is shewn in Figs. 141 to 145[1]. At the highest level was the charging floor *a* on which the pyritic residues and the salt were stored, to be ground in the two mills *b*, the latter being driven by an engine *c* of 12 H. P. The ground charge was run in cars on a narrow gauge tramline to the hoppers of the three calcining furnaces *d*. The gas for heating the latter was generated in the producers *e*; the gaseous products of combustion and calcination passed through the flues *i* into the coke-tower *k* and thence to the stack *y* which also worked the boilers *r*; the latter supplied steam to the engine *c*, for heating the solutions, and for raising them by means of injectors

[1] Braüning, *loc. cit.*

The calcined ores were leached in the tanks *n* lined with lead, and the copper was precipitated from the solution by means of iron in the

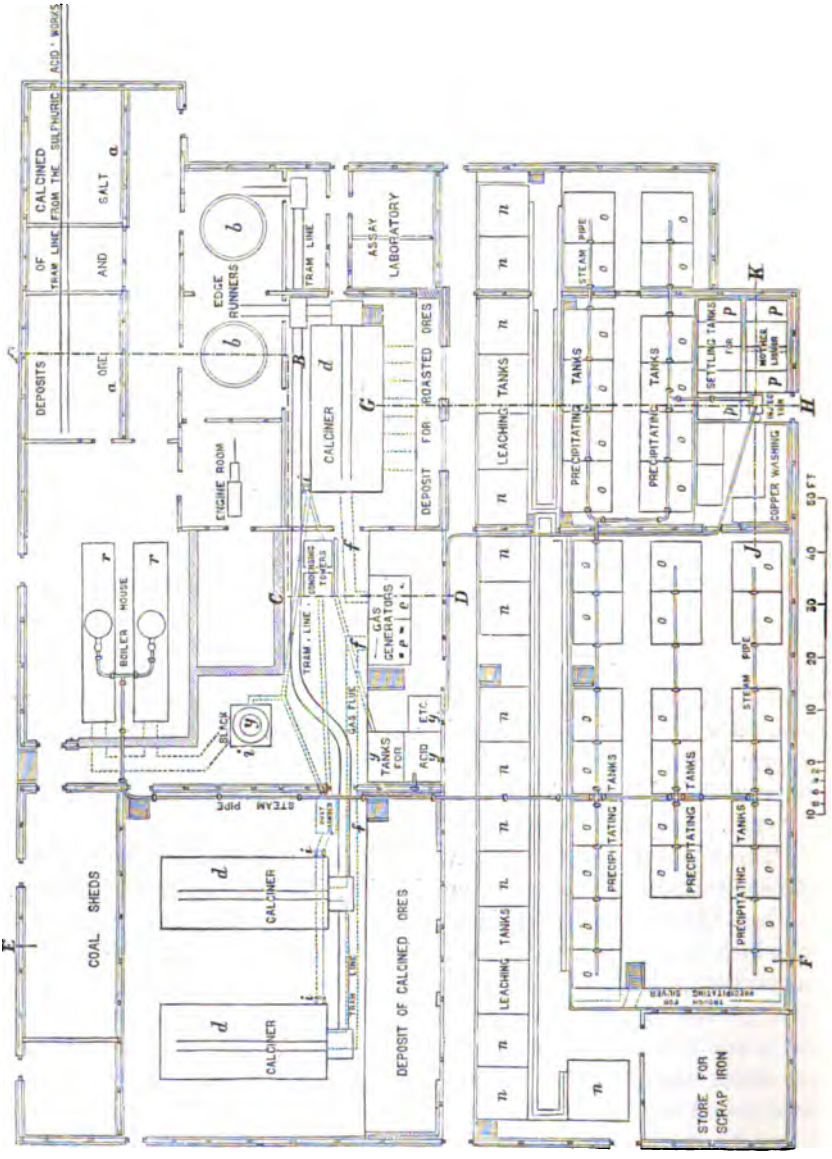


FIG. 141.

precipitating tanks *o*, which were also lead-lined. To hasten the precipitation, the solutions were heated by live steam. The copper-free solutions ran into the reservoirs *pp*, whence they could again be

Section on ABCD

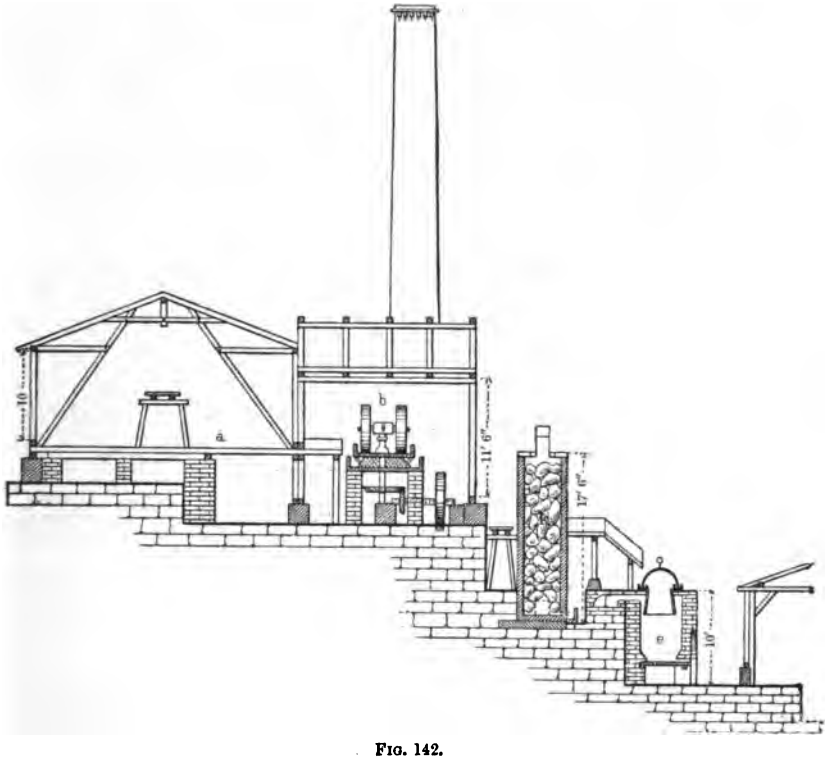


FIG. 142.

Section on J K

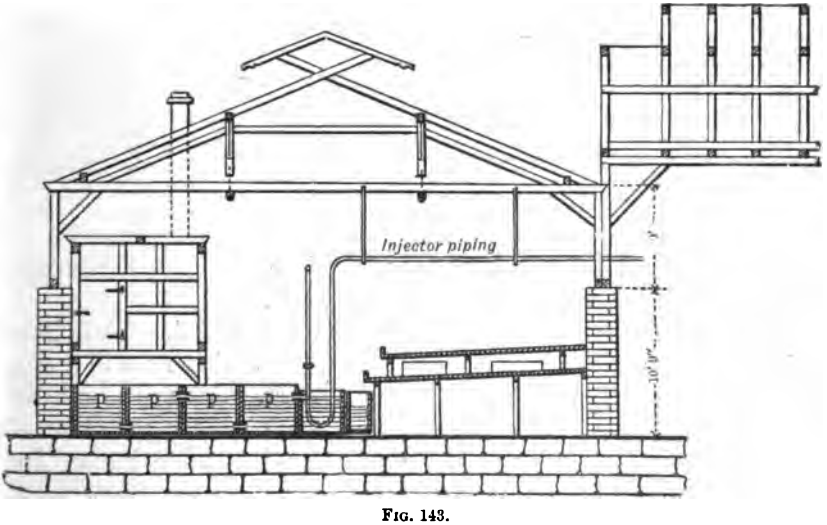


FIG. 143.

raised by injectors to the leaching vats. The dilute acid collected in the coke-tower was warmed in special vessels and was used for a second lixiviation of the ores, to dissolve out the cuprous chloride and cupric oxide.

A reverberatory furnace with rotating bed, fired by means of a grate, the furnace of Gibbs and Gelstharpe, of which pattern there are

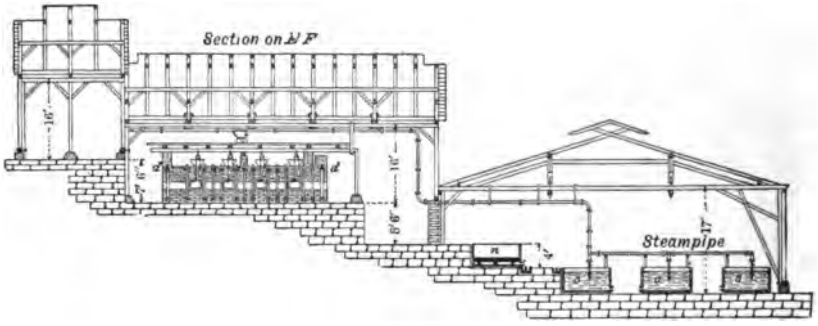
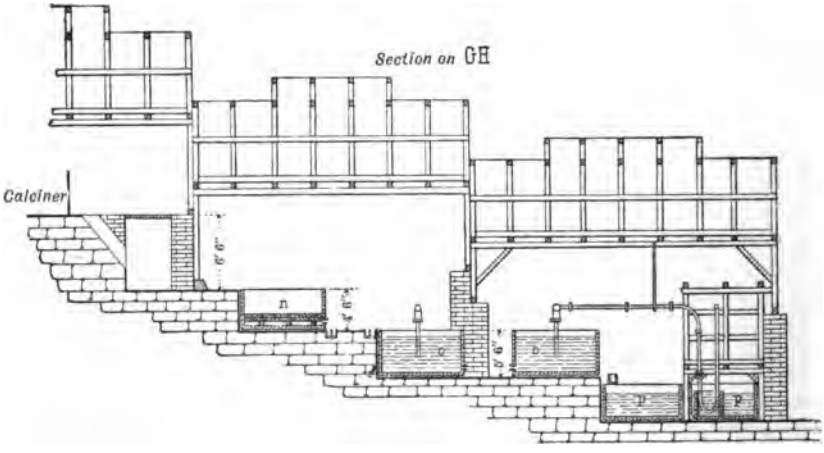


FIG. 144.



IG. 145.

12 in operation at the Bede metal works in addition to the furnace already described, is shown in Figs. 146 to 149.[1]

The rotating bed consists of a circular pan *zz* of boiler plate lined with firebrick; it is carried by a vertical shaft *w* that rests in a step and passes also through a bearing which is stayed by the bent iron pipes *x*. The step is constantly supplied with oil by means of a small pump driven off the main engine, the excess oil running back. The

[1] Lunge, *Soda Industrie*, i. p. 555.

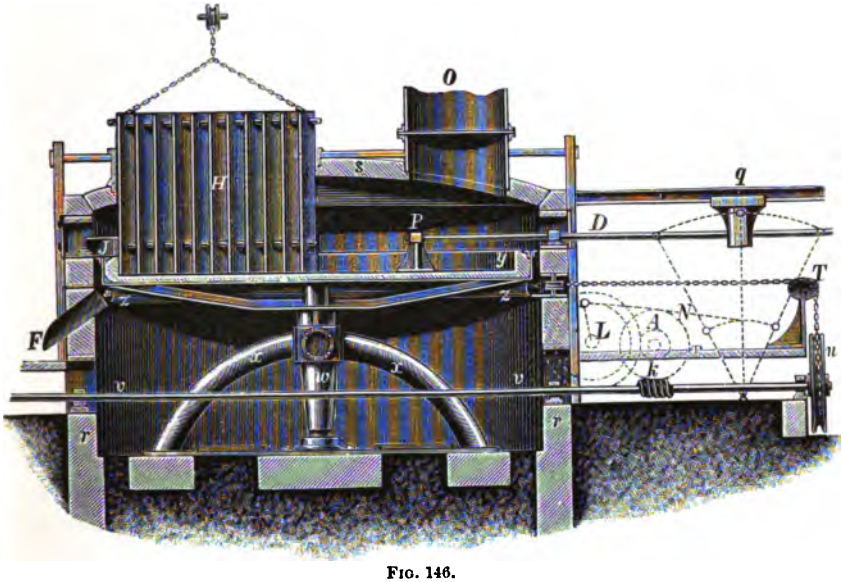


Fig. 146.

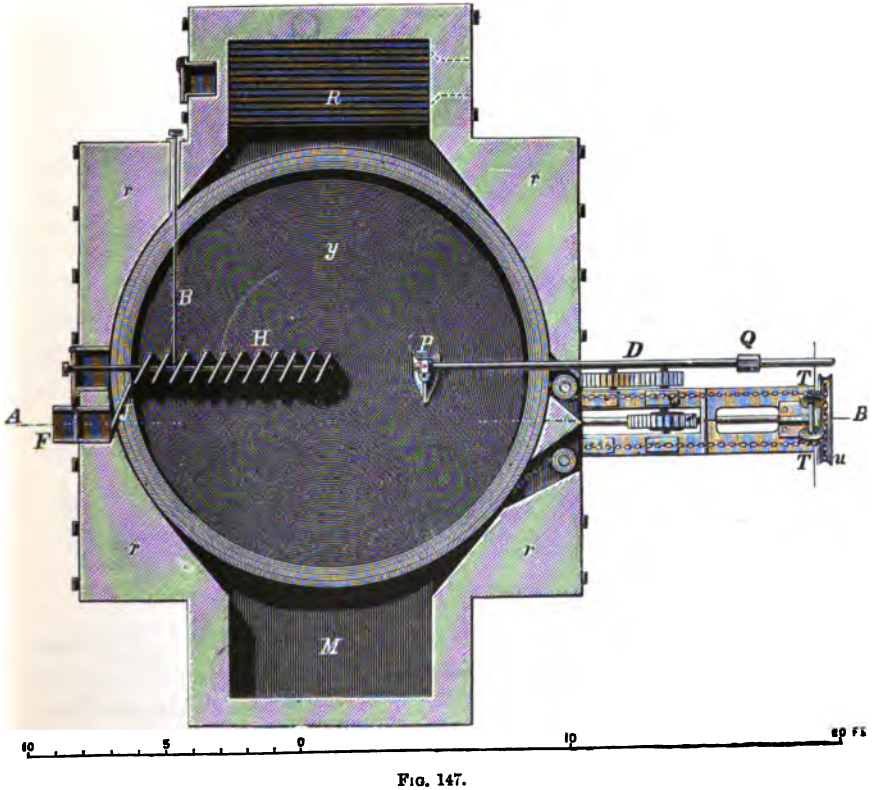


Fig. 147.

pan is driven by an endless chain that grips on a groove running round the pan. The chain is driven by the shaft *v* by means of the pulley *u* and guide pulleys *T*. The movable bed forms the floor of the furnace body, the roof being formed by the arch *s* and the sides by

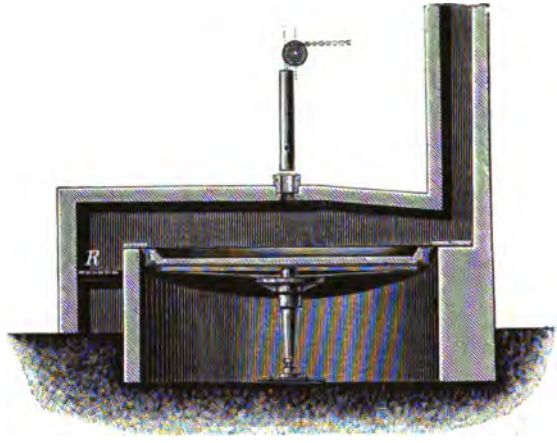


FIG. 148.

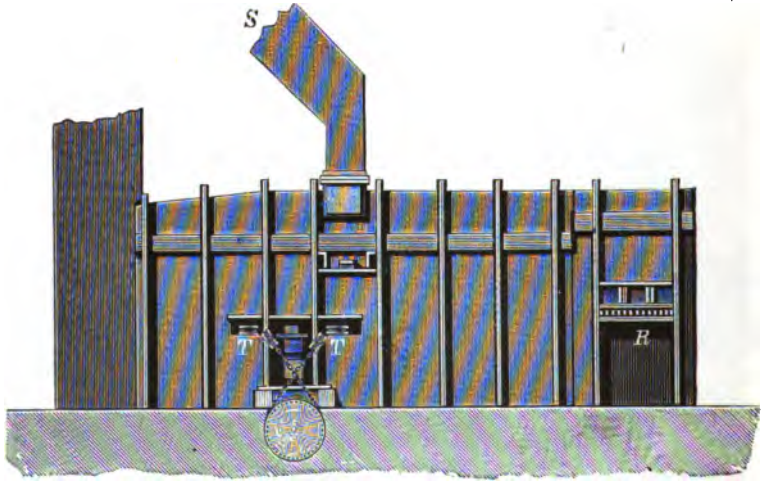


FIG. 149.

the masonry *r*. *R* is the fireplace, and *M* the flue through which the gases escape to the coke-tower. Between the circumference of the pan and the side walls of the furnace there is a clearance of one inch; this gives the bed free play and admits the air requisite for the calcination. The furnace is charged through the opening *O*, furnished

with a hopper and capable of being closed when required. The charge is rabbled by the plough *P* which is attached to the rod *D* and receives a slow back and forwards movement in a radial direction. The plough makes a complete stroke in either direction during one complete revolution of the bed and by this simultaneous movement the ore is sufficiently rabbled and brought into contact with the air. The plough is moved by the tangent screw *k* which works the toothed wheels *A* and *L*. The wheel *L* by means of a crank pin and connecting rod *N* moves a lever, which, by means of the crosshead *q*, moves the rod *D* to which the plough is attached, and communicates a reciprocating movement to it.

The furnace is emptied by means of the grating H, which hangs above the roof during the process of calcination, and is lowered down to the bed when required by means of a chain, through a slot in the roof that can be closed as desired. The grating consists of a series of parallel, very stout strips of boiler iron, which stand diagonally in place in the furnace in which position they are maintained by the rod *B* which is pushed in from the outside. As the bed turns, the ore is pushed through the intervals between the strips of iron, in such a direction that it comes opposite the next pair of openings nearer to the periphery; thence the next turn of the bed brings it still nearer the outside circumference, until it is finally pushed against the plate *JJ* in front of the working door; this forces it into the gutter *F* and thence into a receiver outside the furnace. The cast iron plough lasts a fortnight.

Twelve of these furnaces are driven by two steam engines of 18 I. H. P. each. Each furnace roasts 5 tons of ore with 7½ per cent. of salt in 9 hours. These furnaces admit of very uniform heating and perfect calcination, as the latter is rendered independent of the skill of the workmen. They produce a larger proportion of salts soluble in water than do handworked furnaces. According to Gibb, ore submitted to a chloridising roast in these furnaces contained :—

	Per cent.	Copper per cent.
Cupric chloride	6·70	3·15
Cuprous chloride	0	0
Cupric oxide	0·32	0·25
Sodic chloride	0.90	—
Sodic sulphate	14·03	—
Insoluble copper	—	0·13
Total copper		3·53

A muffle furnace, such as is used in the works of the Tharsis Sulphur and Copper Company, is shown in Figs. 150 to 152.

R R are two grates; *W* is the muffle. The flame first passes over the muffle through the flues *v*, then descends and passes in the opposite direction under the muffle through the flues *z z*, when its direc-

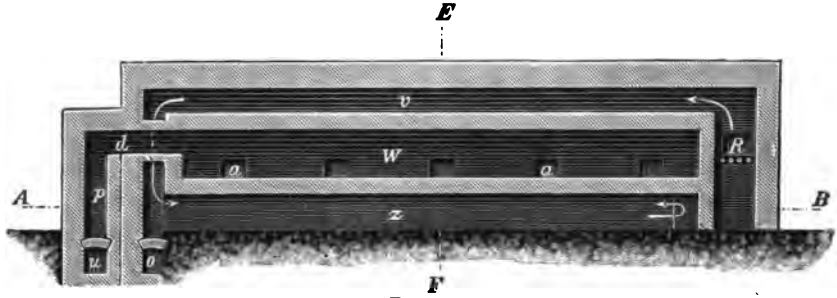


FIG. 150.

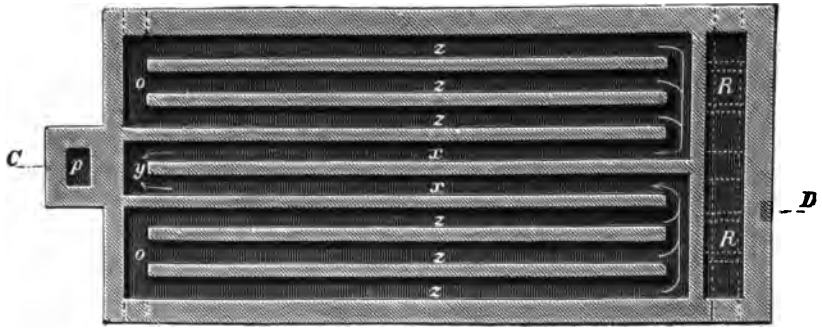


FIG. 151.

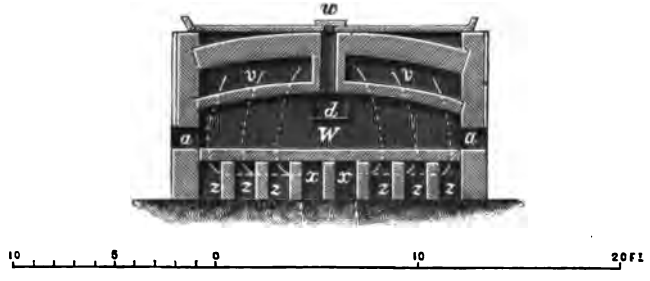


FIG. 152.

tion is again reversed and it returns along the flues *x x*, and descends through the vertical flue *y* into the flue *o* leading to the stack. The gases produced during calcination, which contain chlorine and hydrochloric acid, escape through the flue *d* and the vertical flue *p* into *u*

which leads to the coke-towers. The doors *a a* in the long sides of the furnace serve for working, for air admission and for discharging. Above the furnace is an iron pan in which the mixture of ore and salt is first heated. In this there are a row of apertures *w* provided with covers, through which the charge drops into vertical flues and thence into the muffle. These furnaces consume from 1½ to 2 times as much fuel as reverberatory furnaces, but admit of steadier working and yield more concentrated gases. Calcination lasts 12 hours, 9 hours first with 12 per cent. of salt, and 3 hours more with an additional 8 per cent. of salt.

According to Gibb, ore calcined in these furnaces contained :—

	Per cent.	Copper per cent.
Cupric chloride	4·25	2·00
Cuprous chloride	0·35	0·21
Cupric oxide	0·88	0·70
Sodic chloride	3·40	—
Sodic sulphate	17·40	—
Insoluble copper	—	0·12
Total copper		3·03

For 12 furnaces, one coke tower 8 feet square and 40 to 50 feet high is sufficient; the solution that collects in it consists of dilute hydrochloric and sulphuric acids, the latter being produced by the action of chlorine upon the sulphur dioxide evolved in calcination. This solution is used for dissolving cuprous chloride and cupric oxide out of the calcined ores.

At Königshütte, in Upper Silesia, muffle furnaces with a single bed, fired by a grate, are in use. The larger furnaces have a bed 31 feet 9 inches × 9 feet 6 inches = 305 square feet, and the smaller ones 31 feet 6 inches × 7 feet 3 inches = 228 square feet. In these furnaces calcined Rio Tinto pyrites with 5 per cent. of copper and 3 to 4 per cent. of sulphur, is roasted with 10 to 12 per cent. of salt. The charge, including the salt, is 4 tons 4 cwt. in the larger, and 2½ tons in the smaller furnaces. The roasting takes 9 hours, and the whole operation, including charging and drawing, 9½ to 10 hours. The fuel consumption is 27 to 30 per cent. of the weight of the calcined ore. The gases evolved are utilised as in the last instance.

b. DISSOLVING THE COPPER OUT OF THE ORES

Solution of Copper as Sulphate

The solution of copper that has been converted into sulphate is performed in the same way as has been described, page 208, for ores that contain sulphate of copper.

At Rio Tinto and Tharsis the vessels for dissolving the sulphate, produced as described, are tanks of masonry cemented inside, 98 feet 6 inches long, 32 feet 9 inches wide, and 5 feet deep, with a false bottom made of planks. The liquor runs through the open spaces left between the planks, on to the inclined true bottom of the tank, and escapes through plug holes in the angles of the deeper side, whence it runs into settling tanks. The first leaching is performed with water, which must completely cover the ore, and which is allowed to stand from 2 to 6 hours, according to the richness of the ore in sulphate.

In the following lixiviations the ore is left under water for 8 to 10 hours, there being usually 5 to 6 lixiviations, but sometimes even more. The various solutions mix in the settler, their average contents of copper being 8·5 to 17 lbs. to the cubic yard of solution. The leached ores still retain 0·4 to 0·5 per cent. of copper as sulphide.

At Agordo the crusts from kernel-roasting were leached in wooden tanks of 1,400 to 1,760 cubic feet capacity. First weak and then strong solutions were employed, the solutions being allowed to act for 24 hours on the ores. The richer solutions had a density of 31° to 34° B., the poorer of 14° to 15° B. After three leachings, the residues were used to cover heaps for kernel-roasting, and were then again leached repeatedly. The residues were then sifted, the finer portions containing 0·25 to 0·30 per cent. of copper being thrown away, whilst the coarser were again used to cover roast-heaps, and were then again leached.

Solution of Oxide of Copper

Copper oxide, produced by calcining the sulphide, is dissolved in the same way as when it occurs in ores (see page 199). Dilute acids or ferrous chloride are used as solvents.

At Ore-Knob, North Carolina, the calcined ores which contained 7·75 per cent. of copper oxide, and 4·15 per cent. of sulphate were treated in wooden vats with raised conical bottoms, 6 feet 6 inches in diameter, and 5 feet 3 inches high, with ferrous chloride solution of 22° B. The charge was 1½ tons. The solution (1,500 gallons),

which stood 18 to 30 inches above the level of the crushed ore, was heated by means of steam to 70° C., stirred with the ore for 8 hours, and drawn off after being allowed to settle for 4 hours. Flat-bottomed vats, with filters composed of a bed of sand covered with a bed of coke, were also used, the solution being in this case allowed to stand for four days on the ores.

Solution of Chloride of Copper

Chloride of copper, produced from sulphide in the wet way by means of ferric chloride (by the Dötsch process) is brought into solution by repeatedly watering the heaps with ferric chloride solution, as has been described under the head of that process at Rio Tinto (see page 217). The solution, that flows from the heaps there, contains 8·5 to 12 lbs. of copper to the cubic yard.

Chloride of copper produced in the wet way by means of ferrous chloride and hydrochloric acid, as at Stadtberge, is leached in wooden tanks of the same construction as are used for saturating the ore with the chloridising solution. The leaching liquor is allowed to stand 2 to 4 inches above the level of the ore; 12 to 16 lixiviations are employed, each one lasting 24 hours. The actual solvent is the final mother liquor, to which a certain amount of hydrochloric acid is added in the proportion of 165 lbs. of acid to each 5 tons of ore. The liquor used for fresh ore is the liquor that runs off when the ore is being saturated with ferrous chloride and hydrochloric acid. This contains sufficient free acid to dissolve the oxychlorides of copper contained in the ore; it is saturated after 24 hour's action. It is then drawn off, and a solution run on that has stood once over almost exhausted and once over half-exhausted ores. The first four liquors are precipitated directly, the amount of copper in these solutions being as follows:—

First liquor . . .	2,100 to 2,800	grains	per gallon.
Second „ . . .	1,400 „ 1,750	„	„
Third „ . . .	1,050 „ 1,400	„	„
Fourth „ . . .	700 „ 1,050	„	„

The following liquors, which generally receive a second addition of hydrochloric acid, are enriched as regards their copper contents before they are precipitated. There is 0·4 per cent. of copper left behind in the ores. After lixiviation they are again treated with a cemented cupriferous solution, to remove the last soluble particles of copper from them.

The solution of chloride of copper, that has been produced in the dry way, is performed in tanks or vats of wood, the joints of which

are made good with red lead or tarred hemp, and the entire structure painted with hot tar. At Oker the tanks are lined with sheet lead. These vessels hold 5 to 10 tons; when tanks are used, they are usually about 11 feet square, and 4 feet to 5 feet 3 inches deep. The false bottom is usually made of perforated planks, resting upon boards placed on edge; upon this there is generally a filter of coke or of sifted ashes covered with a layer of heather, or, as was the case at Oker, a single layer of straw.

The floor of the leaching and precipitating house is asphalted and laid on a slope, so that any solution leaking from the tanks may be collected in special receivers. The solutions are run through clay or india-rubber tubes, the latter of which may be closed by pinchcocks. The solution is transferred from one vessel to another by means of injectors.

The calcined ore is thrown hot into the leaching vessels, and treated successively with weaker liquors, or with mother liquors from which the copper has been precipitated, then with hot water as a rule, and finally with the acid water from the coke towers in order to dissolve cupric oxide and cuprous chloride; if there is not sufficient of the latter solvent, dilute hydrochloric or sulphuric acid, that would then have to be bought, must be used. Generally there are three lixiviations with water, and six with dilute acids. The various weak liquors are run on to copper-bearing ores until they have dissolved a certain amount of copper and are neutral. The liquors should not remain too long on the ore, if possible only a few hours.

At Oker, the leaching tanks held 5 tons of calcined ore; the first lixiviation was with end-liquor, which dissolved the cupric chloride, and by virtue of its contents of alkaline chlorides and ferrous chloride, also the silver existing as silver chloride and a great part of the cuprous chloride. The original solution had a density of 18°B and contained in 100 parts:—

Cu	0·015
Pb	trace
Fe_2O_3	0·15
Al_2O_3	0·11
ZnO	0·06
MnO	0·31
CoO and NiO	0·01
CaO	0·12
MgO	0·52
Alkalies	2·61
Cl	2·56
SO_3	5·89

This liquor was allowed to percolate through the ore as long as the escaping fluid still showed any blue colour. The first lixiviation was finished in 4 to 5 hours; 100 parts of the copper liquor thus produced, contained:—

Cu	3·71
Pb	0·01
Ag	0·005
Al_2O_3 } Fe_2O_3 }	0·29
ZnO	4·97
MnO	0·58
CoO and NiO	0·04
MgO	0·27
Alkalies	10·60
Cl	12·56
SO_3	8·95
As and Sb	trace

The first lixiviation dissolved 75 to 80 per cent. of the copper. For the second, the acid liquors from the coke tower were used; these were raised to the boiling point by the introduction of steam, and were then allowed to act for 24 hours upon the ore. The operation was then finished with sulphuric acid diluted to 8° B, 2½ cwt. of chamber acid at 50° B being used for each 5 tons of ore. This last solution was allowed to stand over the ores until it gave a neutral reaction, in consequence of its neutralisation by the various bases, which generally occurred after 2 days.

This last solution contained in 100 parts:—

Cu	0·58
Fe_2O_3 and Al_2O_3	2·13
ZnO	0·06
MnO	0·12
CoO and NiO	0·02
CaO	0·07
MgO	0·04
Alkalies	0·62
Cl	0·13
SO_3	2·39

The residues after leaching, being very rich in iron, were used as flux in the lead works of the Upper Harz, whereby the small amount

of copper still left in them, was extracted. The following was the composition of these residues at Oker :—

Fe_2O_3	79 per cent.
Al_2O_3	3 „
MgO and Alkalies	1 „
CaO	2·5 „
SO_3	5·5 „
Insoluble residue	6 „

Generally such residues, known as "purple ore" or "blue billy," are used when not too impure as iron ores in the blast furnace. On account of their pulverulent condition they can only be used in admixture with true iron ores in relatively small proportions. Quite recently they have been utilised as ores in block form; the residues are ground with 4½ to 6 per cent. of clay in edge runners, moulded by hand into bricks, dried and fired in kilns, whereby a coherent block is produced. Large quantities of purple ore have been used for fettling puddling furnaces; its composition is shown by the two following analyses :—

	I.	II.
Fe_2O_3	90·61	95·10
Cu	0·15	0·18
S	0·08	0·07
P	—	—
$Pb SO_4$	1·46	1·29
$Cu SO_4$	0·37	0·49
$Na SO_4$	0·37	0·29
Na Cl	0·28	—
Insoluble	6·30	2·13
	99·62	99·55
Metallic iron	63·42	66·57

c. THE PRECIPITATION OF COPPER FROM ITS SOLUTIONS

The precipitation of copper from solutions has already been treated of on page 205, and needs but few additional remarks here.

From Cupric Sulphate

At Rio Tinto the sulphate liquors pass first into settling tanks, and then into cemented and asphalted tanks of masonry, 49 feet long, 6 feet wide and 3 feet 3 inches deep; eight or ten of these tanks are so grouped together that the solution traverses them one after another. From these tanks it runs through inclined troughs, 3 feet 3 inches to 6 feet 6 inches wide, 1 foot 4 inches to 1 foot 8 inches

deep, and some miles in length. These troughs are built like the tanks of masonry and cemented inside. Their inclination at the commencement is 0·3 to 0·4 per cent., but ultimately becomes as much as 1·5 to 2 per cent. These precipitating troughs and tanks are filled with pigs of iron; after traversing this system, the solution escapes at the end of the line of troughs, free from copper. As much of the escaping mother liquor as is required, is pumped back on to the ores that are undergoing lixiviation, by means of pumps constructed of an alloy of 80 parts of copper, 15 of lead, and 5 of tin.

It is evident that in this method of precipitation, the consumption of iron must be very high owing to the formation of ferric salts, and that the cement copper must be greatly contaminated with basic salts of iron. The consumption amounts to 2½ tons of pig-iron to the ton of copper. The cement copper after repeated cleansings only contains 60 to 85 per cent. of copper.[1]

At Agordo the liquors containing sulphates were, in accordance with a suggestion of Zoppi, treated before precipitation with sulphurous acid, so as to reduce the ferric to ferrous salts. The consumption of iron for precipitation was thus lessened, 2·5 parts to 1 of copper being required instead of 3·27. Moreover arsenic acid was reduced to arsenious acid, from which iron precipitates metallic arsenic, which could be removed from the copper by washing. The solution to be thus treated was allowed to trickle down a stack, 30 feet high, placed above the precipitating tanks, and provided with horizontal partitions, up which gases from the shaft furnaces are allowed to ascend.

The objection to this process is that sulphurous acid by the reduction of ferric to ferrous salts, becomes itself converted into sulphuric acid, which in its turn dissolves the iron. The consumption of iron, when this method is used, namely 2½ parts to 1 of copper, is still high, and the process has accordingly not been further employed.

The precipitating tank is made of larch wood, 13 feet long, 10 feet wide and 5 feet high. The solution is heated by the heated gases produced in a fire place consisting of a bell inside the precipitating tank provided with a fire grate; the bell is made of sheet lead on an iron frame; the products of combustion traverse iron pipes and boxes that pass through the precipitating tank.

Precipitation from Solutions of Chloride of Copper

Copper is precipitated from solutions that contain it as chloride, by means of iron; sulphuretted hydrogen is only occasionally used.

[1] Knab, *op. cit.* p. 141.

The more cuprous chloride the solutions contain, the less proportionately is the consumption of iron, thus:—

$$CuCl_2 + Fe = FeCl_2 + Cu$$
$$Cu_2Cl_2 + Fe = FeCl_2 + 2Cu$$

If the ores originally contained silver, this will also be in solution as chloride, chloride of silver being soluble in brine; the silver is thrown down at first with the copper and can be extracted if the cement copper first precipitated is collected separately. Or else it may be thrown down before the copper by means of sulphuretted hydrogen, sulphides of the alkalies or alkaline earths, or by iodide of potassium or sodium, as sulphide or iodide as the case may be.

At Rio Tinto the precipitating tanks are of brick, lined with plaster of Paris and inside this with asphalte or Portland cement; they are 6 feet 6 inches wide and 2 feet 6 inches deep. The solutions traverse a series of these tanks. The consumption of iron is 1·12 parts to 1 of copper, and the resulting cement copper contains 80 to 85 per cent. of metal.

At Stadtberge, the copper is precipitated by means of iron in the manner described on page 207. The solution must be clear and feebly acid; when it is neutral, the precipitation is slow and the cement copper produced is slimy, whilst if very acid, the consumption of iron is high. The iron is used in the form of sheet clippings and there must always be some fresh iron put in with the iron that has been partly dissolved, because it takes some time before it is freed from the layer of oxide and rust that covers it. It is therefore added at frequent intervals. In this apparatus from 318 to 424 cubic feet of solution are precipitated in 15 to 24 hours; the consumption of iron is 105 parts to 100 of copper. The silver is precipitated with the copper, and its precipitation takes place in the first third to the first half of the total time occupied. This circumstance is made use of in order to obtain cement copper rich in silver, by running the solution, after the silver has been thrown down during the first half or third of the time, into a second precipitating tank, in which the further precipitation of the copper is completed. The copper in the first precipitation tank is rich in silver.

At Oker the copper was precipitated in wooden tanks lined with lead. The solutions were heated by live steam being led into them in order to hasten the precipitation; they had to be boiled up 2 or 3 times according to their degree of concentration, before all the copper was precipitated. The time occupied was 1 to 3 days according to the amount of copper in the solutions. Wrought iron was used for

the precipitation, the consumption being 1 part for each part of pure copper. The cement copper was removed from the precipitation tanks every four weeks. The position of these tanks is shown in Fig. 141 page 228.

At the Bede Metal Works, the copper is precipitated by means of ground iron sponge; the latter is made from the exhausted ore

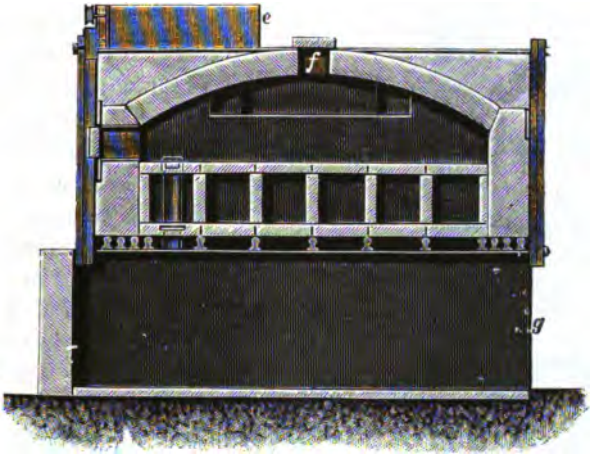


FIG 153.

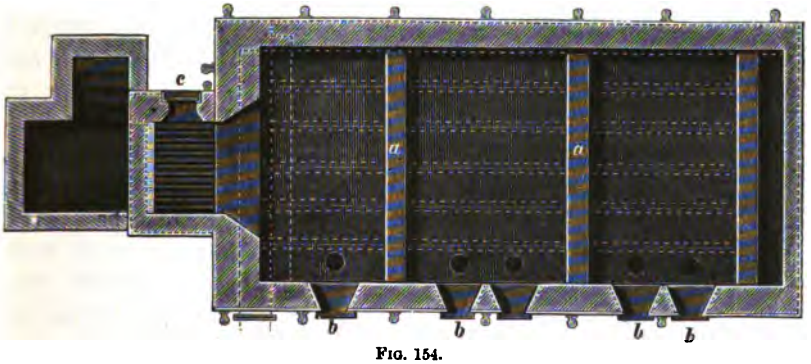


FIG. 154.

residues by means of coal in reverberatory furnaces. The reduction takes place at so low a temperature that the iron does not become fluid, but separates out as a spongy mass. The furnace, which is shown in Figs. 153 to 155,[1] has three divisions formed by means of brick partitions, *a*, each of which is charged separately. The flame which is rendered as reducing as possible by means of a deep-lying

[1] Lunge, *Soda-Industrie*, pp. 571—573.

fire-grate, first passes over these divisions, which are open above, and then traverses 5 flues below the bed of the furnace in order to heat them from below. The charge for each division is 1 ton of purple ore and 6 cwt. of coals that have passed through a sieve of 8 meshes to the inch. This is charged through apertures *f* in the roof, spread out so as to form a layer 6 inches deep on the bed, and, after reduction is complete, the product is raked through vertical flues *h* opening in the bed of the furnace, and which are kept closed during the operation. They are situated close to the working doors *b*. The reduced ore is received in iron boxes placed under these flues, and capable of being closed tightly. The time occupied by the reduction at a full red heat is 9 to 12 hours in the division nearest the fire-bridge, 18 hours in the next, and 24 hours in the last. The charge must be stirred during the operation to keep it from fritting together. The doors of the furnace must be shut air-tight during the reduction so that all air enters through the grate. The reduced ore is allowed to cool for 48 hours in the iron receivers which are closed air-tight. The sponge is then ground under heavy edge runners.

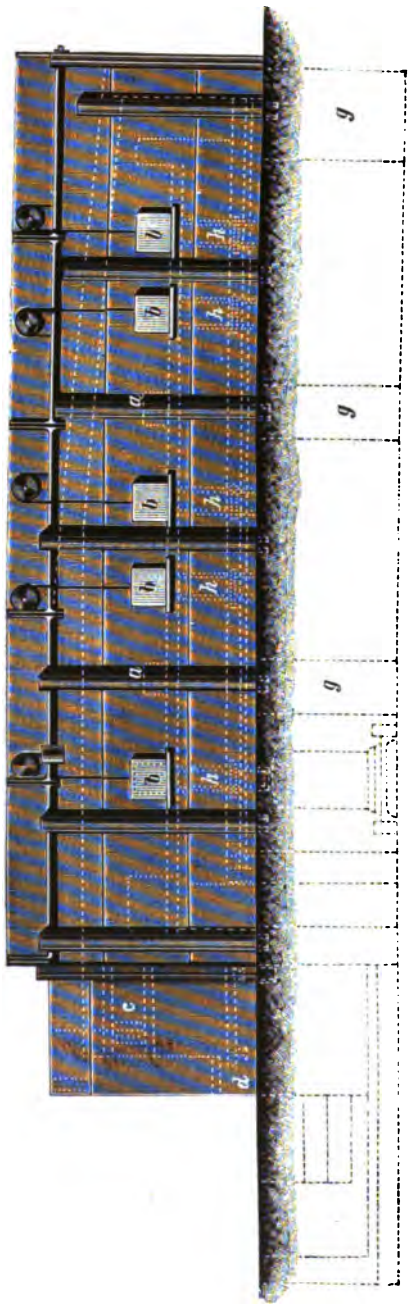


FIG. 155.

The sponge is continually stirred in the copper liquor, this stirring being performed by hand labour, mechanical stirrers, or a blast of air.

Precipitation by iron sponge is open to the objection that the cement copper produced is contaminated by unreduced oxide of iron, coal ashes and coal. It has therefore not been applied in other places.

At the Bede metal works, the copper was also for some time precipitated as sulphide by means of sulphuretted hydrogen according to a method of Gibb. The sulphide of copper produced was washed in a filterpress and compressed, and then smelted like rich matte in reverberatory furnaces, that is to say it was smelted for white metal and blister copper. The sulphuretted hydrogen was produced by treating sulphide of sodium with carbon dioxide, generated by burning coke in a shaft furnace. The sulphide of sodium was made from the acid mother liquor from which the sulphide of copper had been precipitated by evaporating it to dryness in a reverberatory furnace, mixing the residue with coal-dust and reducing it in a similar furnace. The molten product, consisting of sulphide and carbonate of soda, was leached, and the solution, as stated above, treated with carbon dioxide, carbonate of soda being a bye-product of this process. It has however been given up, because it came dearer than precipitation by iron.

The following analyses show the composition of cement copper:—

Precipitated from sulphate solutions:—

Agordo.		Rio Tinto.	
Cu	57·95	Cu	51·90
Fe_2O_3	10·95	Ag	2·35
ZnO	1·78	Pb	1·45
Al_2O_3	0·33	Bi	4·95
CaO	1·80	Fe	7·00
As	4·93	Sb	0·50
Water	3·83	As	2·95
Insoluble	12·10	S	5·10
		CaO	0·60
		NaCl	0·40
		Na_2SO_4	1·40
		Sand	5·00
		Carbon	6·40
		Oxygen and loss	16·00

Precipitated from chloride solutions :—

	English cement copper (according to Gibb) precipitated by		
	Iron sponge.	Heavy scrap.	Light scrap.
Cu	67·50	72·50	67·50
As	0·137	0·306	0·100
Ag	0·011	0·046	0·066
Pb	1·30	2·60	1·74
Fe_2O_3	5·15	4·41	7·56
C	5·10	—	—
SiO_2	3·20	—	—

Wittkowitz (Moravia).		Oker (Precipitated by wrought iron).	
Cu	69·45	Cu	77·45
Ag	0·521	Pb	0·63
Au	trace	Ag	0·10
Bi	0·17	Bi	0·006
Pb	1·50	As	0·04
As	1·45	Sb	0·15
Fe	2·77	Fe_2O_3	6·72
Co	0·13	Al_2O_3	0·99
Ni	0·03	Zn	1·02
Zn	0·36	Mn	0·02
SO_3	5·93	Co+Ni	0·03
Cl	1·22	MgO+Alkalies	2·71
P_2O_5	0·20	SO_3	4·58
Na_2O	1·48	Cl	1·19
CaO	2·19	Insoluble	0·61
MgO	0·28	O, moisture and loss	3·654
Water	2·98		
O combined with metals	8·98		

d. CONVERSION OF COPPER PRECIPITATE (CEMENT COPPER) INTO MERCHANTABLE COPPER

Cement copper is a mixture of metallic copper with basic salts of iron, particles of iron, graphite, and at times silica, antimony, arsenic and arseniate of iron.

It is freed as far as possible by washing from these impurities, when a portion of the copper generally passes into the slimes. When

the washed cement-copper is pure, it may be refined direct, otherwise it is smelted in a reverberatory furnace for blister copper, and then refined.

Refining of cement copper is identical with the refining of coarse copper produced in the dry way. Very impure cement copper, such especially as is obtained from acid solutions, as well as the copper-bearing slimes, are sometimes smelted for matte with the addition of raw ores. When cement copper is smelted in England for blister copper, the slag is skimmed as soon as the charge is melted, and the copper ladled into sand moulds.

If the copper contains a large quantity of carbonaceous matter, as is the case when it is thrown down by iron sponge, it must first be heated to redness with access of air before being melted, so as to burn out the carbon whilst a portion of the copper is oxidised. This kind of calcination is also used with copper that contains much arsenic, as at Rio Tinto, in order to remove a portion of this substance in the form of arsenic oxide.

For smelting cement copper containing arsenic for black copper in reverberatory furnaces, basic lined beds have been recommended. As has already been mentioned under the corresponding dry method (see page 151) it is said that less copper is thus slagged off, whilst the bed lasts longer.

At Atvidaberg, cement copper is smelted to coarse copper in reverberatory furnaces fired by gas.

At Stadtberge, the cement copper is washed in a wooden drum 10 feet long and 4 feet in diameter, provided inside with wooden cleats arranged in a spiral, through which passes a stream of water in the opposite direction to that taken by the cement copper; the escaping slimes are caught in settling tanks. Two-thirds of pure cement copper with 90 to 95 per cent. of copper, and slimes with 10 to 25 per cent. of copper, are produced. In 10 hours, 5 tons of cement copper can be cleaned in this apparatus. The cement slimes are agglomerated with quicklime and smelted for black copper in low shaft-furnaces; to 3 tons of prepared slimes ½ ton of refinery slags and ½ ton of slags from smelting cement slimes are added. The black copper thus produced is refined together with the washed cement copper in a refining furnace fired by gas. The charge is 2½ to 3½ tons of cement copper and 1½ to 2½ tons of black copper, which is worked off in 24 hours with a consumption of 30 to 36 cwts. of coal, and 2½ to 3 cwts. of charcoal. The argentiferous copper is cast in the form of anode plates, and the silver and copper parted by electrolysis.

EXTRACTION OF COPPER IN THE WET WAY FROM FURNACE PRODUCTS

This operation is generally a part of the processes for obtaining silver and gold and will be considered under the head of silver. By the wet way, copper is obtained from sulphides, speiss and alloys, not in the form of metal, but of salts.

The Extraction of Copper by Electro-Metallurgical Methods

Since the introduction of dynamos in 1871, vigorous efforts have been made to utilise the electric current in the extraction of copper from ores and furnace products, and attention has been till now directed exclusively to wet methods. Hitherto no experiments on dry processes with definite results have been published. Such important technical and economic results have, however, been attained in the extraction of copper from its alloys, more especially with gold and silver, that many works have adopted this method for the separation of copper from the precious metals with the simultaneous production of extraordinarily pure copper. For ores and mattes on the other hand, success still remains to be hoped for. Very ingenious methods have been proposed by Siemens and Höpfner for the treatment of ores and sulphides, but in spite of the proofs that these methods are technically capable of execution, nothing is yet known about their continuous working on a large scale. The treatment of mattes by means of electrolysis has not yet led to encouraging practical results.

At present, therefore, a conclusive judgment can only be pronounced on the electrolysis of alloys. This should be favoured whenever copper has to be separated from the precious metals, where a good price can be got for the copper, and where power for driving the dynamos is cheap. It could, however, only be justified as a method for the purification of copper, that is to say for refining it without extracting precious metals at the same time, if electrolytic copper commanded a specially high price—as is not the case at present.

The possibility of the profitable extraction of copper from ores and mattes by electrolysis, requires, as already said, to be demonstrated by working on a large scale for a considerable period of time.

We have now to distinguish :—

(*a*). Extraction of copper from ores.
(*b*). Extraction of copper from mattes.
(*c*). Extraction of copper from alloys.

(A) THE EXTRACTION OF COPPER FROM ORES

Under this head the processes of Siemens and Halske and of Höpfner have to be noticed. Both depend on the employment of insoluble anodes, upon the preparation of the copper solutions from the ores outside the circuit, and upon partially counteracting the back electro-motive force of the current, produced by the decomposition of the copper solution by the current, by means of the secondary action of the anion upon the electrolyte.[1]

The action of soluble anodes, by the solution of which, as is well known, back electro-motive force is more or less neutralised, is here replaced by the higher oxidation or chlorination of the electrolyte surrounding the anode, by means of the anion, oxygen or chlorine as the case may be. In both methods, sulphide of copper or copper-bearing ores are dissolved in special leaching vessels outside the electric circuit. In the Siemens and Halske method, the solution is conveyed first to the cathodes of the circuit, where the copper is deposited, and then it passes, partly freed from copper, to the anode where it is regenerated so as to act as a solvent. In Höpfner's method a separate solution of copper is conveyed to both the cathode and the anode; copper is deposited at the former, whilst the solvent is regenerated at the latter.

The Siemens and Halske Process

In this process,[2] the copper in ores, that contain it as sulphide, is dissolved by a solution of ferric sulphate containing free sulphuric acid, in accordance with the equation:—

$$x\mathrm{H_2SO_4} + \mathrm{Cu_2S} + 2\mathrm{Fe_2(SO_4)_3} = 2\mathrm{CuSO_4} + 4\mathrm{FeSO_4} + \mathrm{S} + x\mathrm{H_2SO_4}.$$

The ferric salt is converted into ferrous, sulphur being at the same time separated. The solution thus obtained, which consists of cupric and ferrous sulphates, is now conveyed into the bath, and first to the cathodes of the current, composed of sheet copper, and which are separated by a non-metallic diaphragm from the anodes, which consist of carbon. This diaphragm is necessary, so as to prevent interference with the reactions that take place in the solutions surrounding anodes and cathodes. The current now deposits a portion of the copper from the cupric sulphate at the cathode, whilst the acid radical SO_4 passes to the anode. The solution, deprived of a portion of its copper, and containing the iron in the ferrous state, flows through the porous dia-

[1] Schnabel, *Allgem. Hüttenkunde*, p. 290.

[2] Imperial German Patent, No. 42,243, Sept. 14, 1886.

phragm into the anode compartment, in which the ferrous sulphate is converted into neutral ferric sulphate $Fe_2(SO_4)_3$ by the anion SO_4. The entire electrolytic operation is expressed by the equation:

$$xH_2SO_4 + CuSO_4 + 2FeSO_4 = xH_2SO_4 + Cu + Fe_2(SO_4)_3,$$

so that the original solvent, $xH_2SO_4 + Fe_2(SO_4)_3$ is reproduced at the anion. This solution is again brought into contact with the ores to be leached, and it continues thus to circulate, as long as it is not rendered too impure by taking up other metals from the ores.

Owing to the oxidation of ferrous to ferric sulphate at the anode, a quantity of electrical energy equivalent to the heat of combination developed thereby is generated, which partly counteracts the back electro-motive force produced by the decomposition of the copper sulphate at the cathode. The heat of combination developed for 1 molecule of ferric sulphate, as expressed in kilogram-calories is:—

$$\begin{aligned} &224{\cdot}88\ Fe_2(SO_4)_3 \\ -\ &186{\cdot}40\ 2Fe\ SO_4 \\ +\ &38{\cdot}48\ \text{Calories.} \end{aligned}$$

The heat of decomposition for each molecule of cupric sulphate amounts to 55·96 calories; these latter appear as back electro-motive force, and are diminished to 17·48 cal., by the 38·48 cal., derived from the oxidation of ferrous to ferric sulphate, and which act in the opposite direction. The back electro-motive force, expressed in volts, would, therefore, only amount to 0·38 volt.

Any copper contained in the ore is also dissolved by ferric sulphate.

If any copper is present as oxide, it will be brought into solution by the free sulphuric acid as also by ferric sulphate. The action of the latter is as follows:—

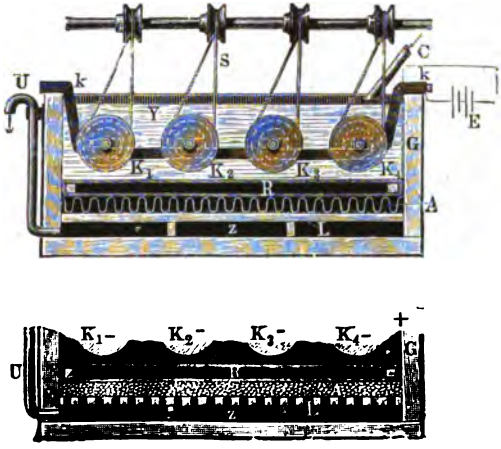
$$3CuO + Fe_2(SO_4)_3 = 3CuSO_4 + Fe_2O_3.$$

Whilst the solution, after being electrolysed and then run through the ore, will, after each leaching, show the same quantities of copper sulphate, ferrous sulphate and sulphuric acid, when the copper is present as sulphide, it will on the other hand, when the copper is present as oxide show a progressive impoverishment in iron and sulphuric acid, together with an increase in the proportion of copper.

To avoid back electro-motive force it is therefore most advantageous that the copper should be present as sulphide, otherwise fresh amounts of ferric sulphate and sulphuric acid have continually to be added to keep the solution at its proper average strength.

As regards the practical execution of the process, it is recommended to calcine lightly ore containing sulphides of iron and copper before it is leached, so as to convert the iron chiefly into peroxide whilst the copper remains for the most part unchanged as sulphide.

The Gerstenhöfer furnace has been recommended for this purpose, but can only be used for pyritic copper ores and then converts the larger part of the copper into oxide. It does not moreover admit of the calcination being regulated and produces much flue dust.



Figs. 156 and 157.

The ore after calcination is systematically leached with the ferric sulphate solution; according to recent experience, the copper can be dissolved from many kinds of finely ground sulphuretted copper ores even without previous calcination if the solution is moderately warmed. Either tanks or revolving drums can be used as leaching vessels. The solution when saturated with copper, and which should then be free from ferric sulphate, is conveyed to the cathodes of the electric circuit.

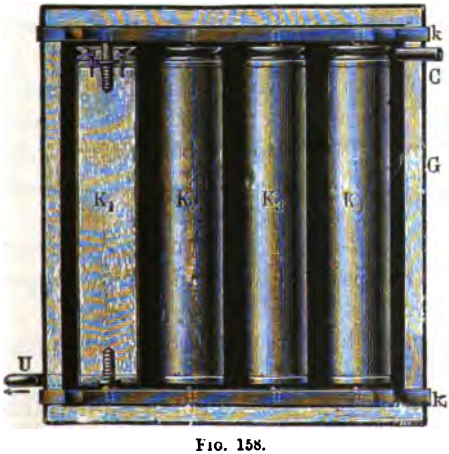


Fig. 158.

In order to divide the decomposing cells into anode and cathode divisions, membranes were at first used, but were found not to answer well, as they either opposed too great a resistance to the current or were rapidly destroyed, were apt to stretch, and allowed the solutions to break through them.

Another form of decomposing cell, shown in Figs. 156 to 158, was

therefore proposed. The bath is formed of a shallow wooden tank, with a false bottom L, upon which rests the anode A connected to the dynamo by means of an insulated conductor ; the anode is made of retort carbon in the shape of plates or of small pieces, the latter contained in a perforated leaden tray. Above the anode lies the filter R made of felt or other suitable material. The cathode division above the filter, contains the cathodes which consist of a series of revolving drums K_1, K_2, K_3, K_4, covered with a conducting surface of sheet copper, and connected by means of copper spindles, with the conductor k, which latter also forms an electrical conductor between the various drums. These latter can be slowly rotated by means of the waterproof cords S.

The copper-bearing solution, which forms the electrolyte, enters the cathode division in such quantity that the drums are always kept covered by it, and it is kept in motion by the rotation of the drums. It passes through the filter into the anode division, and through the false bottom of the latter into the space Z, whence it escapes by the pipe U. The quantity of fluid that escapes is equal to that which enters, so that the fluid is continuously circulating through the bath.

The electric current moves in the opposite direction to that of the solution. It enters the anode through insulated conductors, passes thence through the electrolyte to the cathode drums, from which it passes by the conductor k into the next decomposing cell or from the last cell back to the dynamo. At the cathode the solution loses about $\frac{2}{3}$ of its copper contents, whilst a corresponding quantity of $SO_3 + O$ is set free. The solution, thus deprived of its copper, passes through the filter to the anode where the anion SO_4 reproduces ferric sulphate; the solution of this salt falls to the bottom by virtue of its high specific gravity and escapes first from the anode division, to be again conducted to the dissolving vessels.

The difference of potential is said to be 0·7 volt., and the current density is said not to be greater than is used with anodes of copper matte (13·5 amperes per square yard).

Fresh improvements in the plant have recently been made and will be found described in the catalogue of the Gruson Company at Magdeburg-Bruckau, which undertakes the erection of plant for this process.

In this, the anodes consist of homogeneous, round bars of carbon specially prepared, 109 of which are connected together by having lead cast round them so as to make a system 5 feet 3 inches long by 16 inches wide. The current is conveyed to it by a strip of lead cast on

to one end of the leaden casting. Such a system of anodes is shown in Fig. 159.

The baths, whose construction is shown in Fig. 160, are shallow wooden tanks, made tight by a lining of cloth woven of jute and covered with asphalt. A certain distance above the anode, which

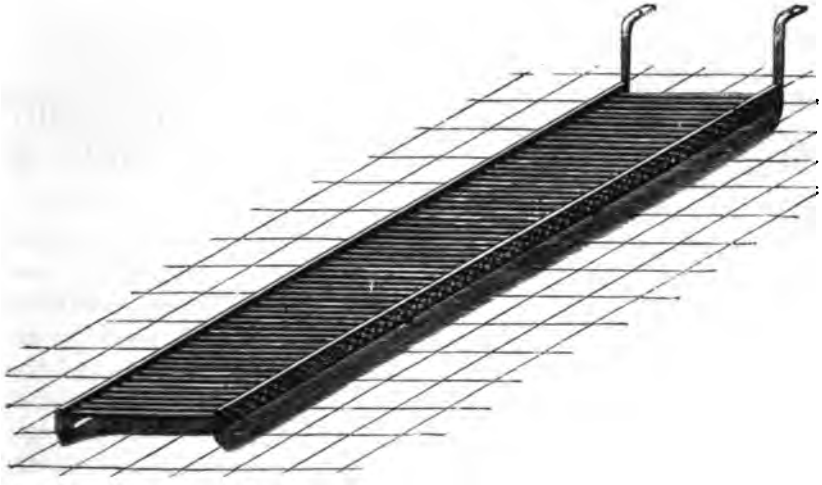


Fig. 159.

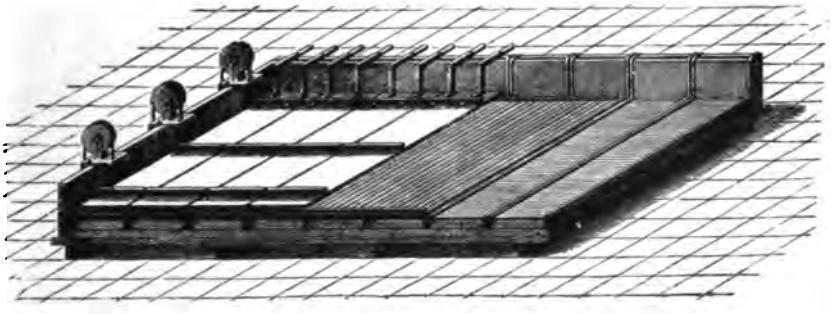


Fig. 160.

lies on the bottom of the tank is a filter of linen stretched on a wooden frame, which divides the bath into the anode division, and the cathode division above it. In the latter lie the cathodes occupying the entire surface of the bath; they consist of wooden plates covered underneath with a thin sheet of copper upon which the electrolytically separated copper is deposited. Between the filter and the cathode plates, there is an arrangement (details of which are

not given) for keeping the solution in movement and thus keeping the solution about the anodes thoroughly mixed.

The copper is to be dissolved out of the ore in trough-shaped

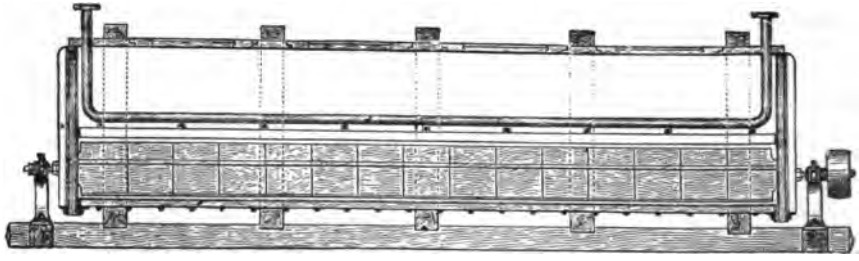


FIG. 161.

wooden boxes, lead-lined, 14 feet 9 inches long, 2 feet 6 inches wide and 3 feet 3 inches high, in the lower portion of which are two stirrers consisting of horizontal square steel tubes covered with lead, to which wooden paddles are secured. The bearings of these tubes and the pulleys for driving them lie outside the troughs; the openings in the ends of the latter, through which the spindles pass, are rendered water-tight by special arrangements. The solution is heated when needed, by a leaden pipe running above the tops of these agitators. The arrangement of these dissolving tanks is shown in Figs. 161 and 162.

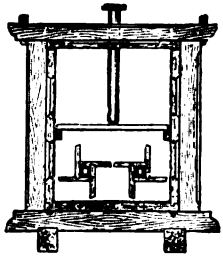


FIG. 162.

The exhausted ore is separated from the liquor in a vacuum filter, shown in Figs. 163 and 164. This consists of an upper wooden box,

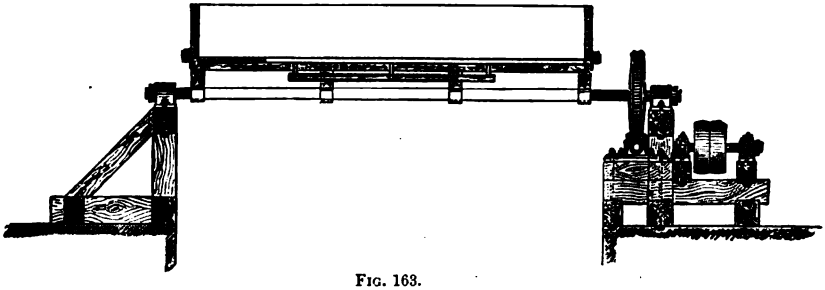


FIG. 163.

lead-lined and open above, to receive the ore to be filtered, and a closed lower box also of wood and lead-lined; the two are separated by a grating which carries a filter cloth resting on a perforated sheet

of metal. By means of an air-pump the air is exhausted from the lower box, so that the solution is forced through the filter by atmospheric pressure, whilst the ore is retained in the upper box. The

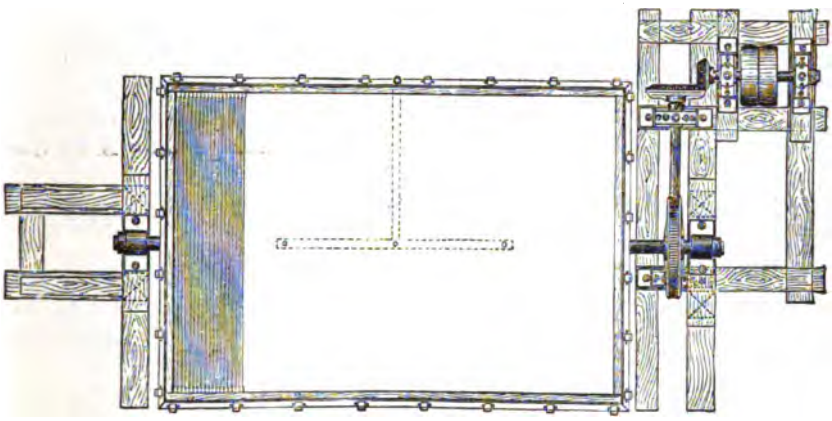


FIG. 164.

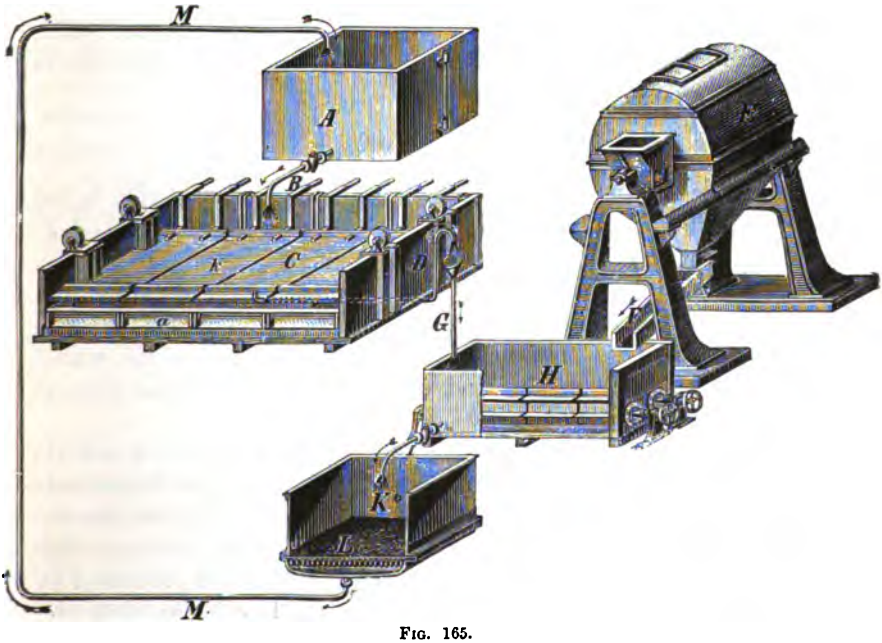


FIG. 165.

whole apparatus is carried on trunnions in a frame, so that after the liquor has been filtered off, the ore in the upper box can be tipped out.

The complete plant is shown put together in Fig. 165. A is the

storage tank for the solution to be electrolysed; the latter passes through the pipe B into the bath C, flows first into the cathode division *k*, and then through the filter into the anode division *a*, from which the escape-pipe D leads it to the pipe G, which conducts it into the solution tank H. Here it comes in contact with the ore to be leached, which has been ground in the ball-mill E. After the copper has been dissolved, the mixture of exhausted ore and liquor runs into the vacuum filter K. The solution aspirated through the latter is again conveyed to the storage tank A by the pipe M.

It is said that 10 hours are required for dissolving the copper out of the ores down to 0·1 to 0·5 per cent.

No definite opinion can yet be expressed as to the commercial value of this process; before this can be done, working results on a large scale, extending over a considerable period, must be available.

Höpfner's Process[1]

In this method a solution of cuprous chloride in sodic or calcic chloride is produced outside the electric circuit, the copper being dissolved from the sulphuretted ores by means of cupric chloride in accordance with the equation :—

$$CuCl_2 + CuS = Cu_2Cl_2 + S$$

The solution of cuprous chloride in sodic or calcic chloride is led to the cathodes, and is made to flow over a whole series of cathodes; a similar solution is led separately to the anodes, anodes and cathodes being separated by diaphragms. The anodes consist of carbon, the cathodes of sheet copper. At the cathodes the cuprous chloride solution is decomposed, copper being deposited at the cathode, whilst chlorine passes to the anodes, and combines there with the cuprous chloride to form cupric chloride.

By the conversion of cuprous into cupric chloride, a certain quantity of electrical energy is generated, which in part counteracts the back electro-motive force produced at the cathode by the decomposition of the cuprous chloride solution. Höpfner estimates this back electro-motive force at 1·8 volts, and the potential generated by the chloridising of the cuprous chloride at 1 volt, so that the electrolysis absorbs a potential of 0·8 volts.

The solution surrounding the cathodes flows past them un-

[1] *Zeitschr. für angewandte Chemie*, 1891, p. 160; Imperial German Patent 53,782, March 2, 1888.

interruptedly, and leaves the bath almost free from copper; the solution surrounding the cathode retains its copper, but the cuprous is converted into cupric chloride. The latter solution also flows in a continuous stream past the anodes and leaves the bath as a solution of cupric chloride, in which state it serves to dissolve fresh quantities of copper from the ores.

The copper is to be dissolved out of the ore by means of a hot solution of cupric chloride, in rotating drums. Any sulphide of silver that may be present will be converted into chloride and dissolved in the liquor. The silver is best precipitated before the solution is electrolysed; arsenic, antimony, bismuth, iron, etc., should also be first thrown down by cupric oxide or caustic lime.

With a potential of 0·8 volt and a sufficient number of baths, one horse power is said to precipitate 96·8 lbs. of copper in 54 hours, allowing a current loss of 10 per cent.

The above process presents the advantage of high efficiency of the electric current, because twice as much copper is deposited from a solution of cuprous chloride as from cupric chloride or sulphate with the same current, and the further advantage that silver is dissolved along with the copper. A yet further advantage is said to be the great solvent power of the cupric chloride solution, a gallon of which is stated to dissolve 1·5 lbs. of copper. The rate of solution however is probably but slow, just as it is when ferric sulphate is the solvent employed.

A disadvantage is the use of diaphragms, which have been found to give unsatisfactory results in the experiments of Siemens and Halske in their own process.

As in the last case so here, no definite judgment about the value of this process can be formed until the results of its working on a large scale for a considerable time are known.

(B) EXTRACTION OF COPPER FROM MATTES

If copper matte be used as the anode of an electric circuit, an acid solution of bluestone as the electrolyte, and a sheet of copper as the cathode, the copper can be deposited on the latter, whilst sulphur remains behind at the anode, and iron is dissolved as ferric sulphate. The electric energy generated at the anode by the solution of the iron and copper in part destroys the back electro-motive force due to the decomposition of the copper sulphate.

The method of Marchese for electrolysing copper matte is founded on the above principles; he uses an anode of copper matte containing iron and an electrolyte produced by treating with sulphuric acid

copper matte that has undergone a sulphating calcination. It has been used at Casarza near Genoa, but has not made any headway. According to Topetti,[1] the Casarza works employ 20 Siemens machines, each of which electrolyses a set of 12 baths with a current of 15 volts and 250 ampères. The matte to be electrolysed contains: copper 30 per cent., sulphur 30 per cent., iron 30 per cent.; it is cast into slabs 1·2 inches thick and 31·5 inches × 31·5 inches in area. By means of strips of sheet copper, 0·08 inch thick and 0·8 inch wide, which are cast into the slabs, the latter are suspended

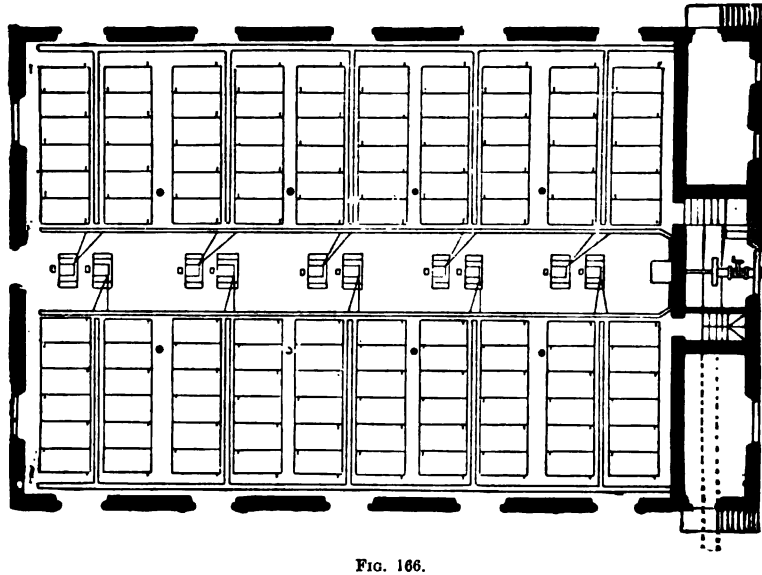


Fig. 166.

from the conductors of the cells. Each cell contains 15 anodes. The cathodes, of sheet copper 0·012 inch thick, and 27·5 inches × 27·5 inches in area, are suspended two inches from the anodes. The conductors are 1·2 inches thick.

The decomposing cells are made of boards 2·75 inches thick and lined with sheet lead; they are 6 feet 6 inches long, 3 feet wide, and 3 feet 3 inches deep. To obtain a ready circulation of the solution they are arranged stepwise one below the other. The arrangement of the cells and their disposition relative to the dynamos are shown in Figs.[2] 166 to 168, Fig. 166 being a ground plan and Fig. 167 a cross section of the establishment.

[1] *Giornale Politecnico, Milano,* November and December, 1885

[2] From the *Lumière Électrique,* xiv. 1884, No. 42.

The solution of bluestone that forms the electrolyte is produced by extracting copper matte, that has been calcined for sulphate, by means of water and dilute sulphuric acid. A solution containing 3 per cent. of copper is said to give the best results. Half of the copper is said to be precipitated from it during its passage through the baths; it is then used for dissolving fresh quantities of copper

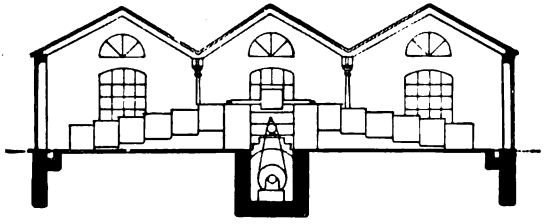


FIG. 167.



FIG. 168

from the calcined matte. The difference of potential of the baths is 1 to 1·5 volts. The anodes are supposed to remain hanging for 3 months in the baths and then to be replaced by new ones. The deposit of copper on the cathodes is said to increase by 2 inches in 3 months and then to be removed; 44 lbs. of copper are stated to be deposited per horse power in 24 hours.

The disadvantages of this process are that casting the anodes is

difficult and uncertain, that they are fragile, and fall to pieces before they are completely dissolved, whereby the electrolytic action is disturbed; that more copper is deposited at the cathodes than goes into solution at the anodes, whereby the electrolyte becomes continually poorer in copper, but on the other hand richer in iron, so that it often needs renewing. The quantity of matte which is used after calcination for preparing the solution is therefore greater than that which can be directly submitted to electrolysis.

The ferric sulphate formed at the anodes has a solvent action on the copper deposited at the cathodes unless diaphragms are inserted. In consequence of the frequent renewal of the electrolytes, the consumption of sulphuric acid is a serious item. The contact resistance at the anodes occasions great losses of current power, and finally the copper obtained is not of as good quality as the copper obtained electrically from alloys of that metal.

Experience has shown that the process can therefore not be recommended for mattes rich in iron, in spite of the increase of current energy produced by the solution of the iron.

Mattes rich in copper and poor in iron could be more cheaply treated in the dry way, and if these mattes contain silver, it would be more advantageous to smelt them for argentiferous copper and only to electrolyse the latter.

(C) EXTRACTION OF COPPER FROM ITS ALLOYS

The electrolysis of alloys of copper with the precious metals has, in the short period since its introduction, been found capable of producing great technical and commercial advantages, and is employed in a large number of works in Europe and America. In 1865 it was introduced by Elkington, who used Welde's magneto-electric machine for generating the current. Then followed the Hamburg refinery under Wohlwill's management with Gramme machines, and then Oker under Braüning's management with Siemens machines. Braüning and the firm of Siemens and Halske deserve great credit for the manner in which they have developed the process with Siemens machines. The method is at present used amongst other places at: Struthütten near Siegen, Stadtberge in Westphalia, Oker in the Lower Harz, Altenau in the Upper Harz, Mansfeld, Moabit (Kaiser), Wittkowitz in Moravia, Stefansbütte in Hungary, Brixlegg in the Tyrol, Kedabeg in the Caucasus, Works of the Russian Copper Company in the Urals, Biache St. Wast in the Pas de Calais, Marseilles (Hilarion Roux and Co.), Swansea and Birmingham in

England, Anaconda and Great Falls in Montana, Bridgeport in Connecticut, Newark in New Jersey, Boston in Massachusetts, Durango in Colorado, Baltimore, Chicago, St. Louis and Brooklyn all in the United States, Wallaroo in Australia. The largest installation that the author has seen was at Anaconda. The process depends upon the facts that, when the alloy, cast in suitable slabs, is used as the anode of an electric current, an acid solution of bluestone as the electrolyte, sheets of copper as the cathode of the current, and when a current of suitable density is employed, the copper will be dissolved from the anode and deposited at the cathode, whilst the silver remains at the anode and falls to the bottom of the bath in the form of mud. At the anode SO_4 is separated and a corresponding amount of copper is dissolved; through this solution of copper, the electric current is reinforced by an amount of energy that to a great extent neutralises the back electro-motive force. The work to be done by the current is therefore comparatively small. When a current of proper density is employed, the metals that are more electro-positive than copper remain in solution, whilst those that are more electro-negative, such as silver, remain at the anode. If the density of the current exceeds certain limits, all the metals present in the anode will be dissolved and reprecipitated at the cathode, producing brittle copper and increasing the outside resistance of the circuit. If the current is not dense enough, cuprous oxide and finally even cupric oxide are precipitated at the cathode. The more neutral the electrolyte becomes, the more readily do the electro-negative metals of the anode pass into solution and the more easily are the electro-positive metals precipitated at the cathode. With brittle and less dense anodes, better results are obtained than with malleable and dense anodes; cast and rapidly cooled anodes are better than when rolled.

Killiani[1] has tried exhaustive experiments on the behaviour of the commonly occurring constituents of argentiferous coarse copper; his results are reproduced below. They refer to a tension of 0·1 to 0·25 volt, a current density of 16·7 ampères to the square yard, electrodes 2 inches apart and an electrolyte containing 1·5 lbs. of blue vitriol and 0·5 lb. of sulphuric acid to the gallon.

Cuprous oxide, being a bad conductor, goes into the slimes, but is slowly dissolved by the acid of the bath.

Cuprous sulphide, when it is present in small quantities, as is usually the case, goes into the slimes. When larger quantities are present, it is decomposed, the copper being dissolved and the sulphur precipitated.

[1] Berg-und Hüttenm. Ztg. 1885, p. 249.

Silver, *Platinum* and *Gold* go into the slimes in the form of powder. If the solution is neutral, silver may also be dissolved, and is then deposited at the cathode.

Bismuth and *Bismuthic oxide* are dissolved, but separate out for the most part as basic sulphate.

Tin is dissolved but is precipitated after some time as basic sulphate. The tin has a beneficial action on the quality of the copper deposited at the cathode. With the above named current density (16·7 amperes to the square yard), copper, if deposited from a neutral solution of chemically pure sulphate, is very brittle and has a warty surface. If the anode however contains a considerable amount of tin the copper will be malleable and smooth. The tension of the bath too is very notably diminished when the anodes contain a considerable proportion of tin.

Arsenic dissolves in acid or neutral solution as arsenious acid; as soon however as the solution is saturated, it is thrown down among the slimes as an arsenite. From a neutral solution arsenic is deposited at the cathode, from an acid one only when it is relatively poor in copper.

If the arsenic exists in the anode as an arseniate, it goes entirely into the slimes in neutral solutions because arseniates are non-conductors of electricity, but in an acid solution it is gradually dissolved as arsenic acid in consequence of secondary reactions.

Antimony is partly dissolved in acid or neutral solutions, and partly remains at the anode as a basic sulphate. The dissolved antimony separates out from the solution as basic sulphate, on being allowed to stand for a considerable time. Antimoniates, that exist in the anode, pass, as nonconductors of electricity, into the slimes, but are slowly decomposed by the acid of the solution with the separation of antimonic acid; the bases which were combined with it tend to neutralise the solution. As long as the solution is acid and contains the above stated amount of copper, even when it is saturated with antimony, none will be deposited on the cathode; at the worst some of the basic salt may mechanically adhere to it. If on the contrary the solution is nearly or quite neutral, antimony will be deposited with copper at the cathode, and the deposit will be more brittle; but even with an acid solution, antimony is deposited with the copper, if the bath becomes impoverished in copper.

Lead is attacked even before copper, and is thrown down among the slimes as an insoluble sulphate. The presence of lead therefore renders the bath poorer in copper.

Iron, *Zinc*, *Nickel* and *Cobalt* are more electro-positive than copper

and therefore dissolve before it does; they impoverish the bath as regards both copper and free acid. *Iron* goes into solution as a ferrous salt, at the low current density required for the electrolysis of coarse copper, and this is gradually oxidised by the air to ferric sulphate.

The ferric sulphate only makes its appearance at the anode with very high current densities, at which oxygen and free acid also form. When the solution only retains 0·02 lb. of copper to the gallon, the rest of its original copper contents having been replaced by iron, the copper at the cathode becomes warty.

Hence the slimes at the anodes may contain :—gold, platinum, silver, sulphide of silver, cuprous oxide, copper sulphide, basic sulphates of bismuth, tin and antimony, antimonic acid, arsenite of copper, arseniates and antimoniates, sulphate of lead and slag, through which latter iron, lime, magnesia and silica may also enter into the composition of the slimes. A little pulverulent metallic copper is also always precipitated.

The anodes are simultaneously attacked at the surface and in their interior.

By taking up iron, zinc, nickel, cobalt, manganese, tin, arsenic, antimony and bismuth, the electrolyte becomes richer in these metals, but poorer in copper and in acid.

The impoverishment in copper of the solution is partly counterbalanced by the fact that an acid solution of sulphate of copper is reduced by copper to cuprous sulphate, which is again oxidised to cupric sulphate by the atmospheric oxygen. By this secondary reaction (which is used in separating copper and silver by so-called sulphuric acid leaching), copper is dissolved as long as the solution remains acid, and the more, the less the current density and the more the solution, in consequence of rapid circulation, comes into contact with the air.

For the process to continue uninterruptedly, it is necessary to keep the bath acid by adding sulphuric acid from time to time and to make good any deficiency in copper by additions of bluestone.

The neutralisation of the solution produced by the absorption of foreign metals from the anode has in many ways a very prejudicial effect upon the electrolytic method; the solution becomes a worse conductor, foreign metals are deposited at the cathode, and cuprous oxide is also deposited along with the copper at the cathode.

The conductivity of the solution diminishes as it becomes neutralised at such a rate that, with electrodes 2 inches apart, and all other conditions unchanged, the difference of potential in the bath rises

from 0·1 volt to 0·25 volt. The above mentioned metals, antimony, arsenic and tin pass into the cathode deposit, and make it brittle. The current density employed no longer suffices to completely decompose the sulphate of copper in the electrolyte, so that a certain amount of cuprous oxide is deposited with the copper at the cathode; this renders the deposit so brittle that it can be ground in a mortar. If the solution is acid, the cuprous oxide will be dissolved by virtue of a secondary reaction; if it is neutral, the latter remains in the cathode deposit.

In order to produce good copper, the solution must circulate as actively as possible, because the copper deposited at the cathode is purer and more malleable, the more rapidly the solution is circulating. If the solution is not in motion, it becomes richer in copper at the anode, but poorer at the cathode; the poor solution ascends in the bath, whereby a layer of solution offering great resistance is introduced into the circuit. This renders it possible for other metals or for hydrogen to be separated along with the copper.

The following table compiled from a number of experiments by Kiliani shows the effect of impurities in the anode or the solution, as also of the movement of the solution upon the difference of potential in the bath. The experiments were performed with electrodes 2 inches apart, and with a current density of 16·7 ampères to the square yard.

One gallon of solution contains	Anode composed of	Tension in volts.	
		Solution in movement.	Solution at rest.
1·5 lbs. crystallised copper sulphate and 0·5 lbs. sulphuric acid	Pure copper	0·095	0·095
	Black copper	0·120	0·120
	Copper matte	0·40	0·40
1·5 lbs. crystallised copper sulphate	Pure copper	0·24	0·243
	Black copper	0·275	0·278
	Copper matte	0·532	0·535
0·08 lb. crystallised copper sulphate, 1·6 lbs. crystallised ferrous sulphate, 0·5 lb. sulphuric acid	Pure copper	0·22	0·75
	Black copper	0·25	0·75
	Copper matte	0·50	1·00
The same without sulphuric acid	Pure copper	0·30	1·10
	Black copper	0·35	1·15
	Copper matte	0·75	1·30

The black-copper contained:—

Copper	96·6 per cent.
Silver	0·403 ,,
Gold	0·011 ,,
Arsenic	1·23 ,,
Iron	1·0 ,,
Sulphur	0·54 ,,

As regards the relation between strength and tension of the current, the same amount of copper can be obtained from a given power with high strength and low tension as with low strength and high tension. It is for instance immaterial whether a dynamo giving 30 volts tension and 120 ampères of current strength or one giving 15 volts and 240 ampères is employed; the only requisite is that in each case the current density shall be the same, *i.e.* that the same current strength is used for a given area of electrodes. The most suitable current strength for the electrolysis of copper is given as between 16·7 and 25 ampères to the square yard. Low tension dynamos require very thick and short leads; with these machines the course of the operation is far more liable to be disturbed by the least increase of resistance in the baths than when higher tensions are employed. For this reason modern machines have greater electromotive force and lower current strengths.

With high strengths of current a smaller quantity of cells, with low strengths a correspondingly larger number of cells are employed.

The following table shows the efficiency of various dynamos of Siemens and Halske at the works at Oker:—

H.-P. of the motor.	No. of pattern of dynamo.	Tension in volts.	Current strength in ampères.	Effective power at the terminals in watts.	No. of cells.	Copper deposited per 24 hours.
						lbs.
7—8	c′	3·5	1,000	3,500	12	551·2—661·4
,,	cF_8	30	120	3,600	80	,,
,,	cH_7	15—20	240	3,600—4,800	40—50	,,

The capacity of certain works using Gramme machines is given on the following page.

The arrangement of a bath for the electrolysis of copper alloys is shown in Figs 169 to 171.

L L are the copper conductors from which the anode plates and the cathode sheets are alternately suspended; the conductors for the former are marked +, for the latter −, and the path of the electric

	Oeschger, Mesdach & Co., Biache St. Waast, Pas de Calais.	Hilarion, Roux & Co., Marseilles.	North German Refinery, Hamburg.
Dynamo	Gramme	Gramme	Gramme
H.P.	8	5	12
Tension in volts	4	8	27
Strength in ampères	700	300	300
Number of baths grouped together	20	40	60
Effective cathode area per bath . sq. feet	227·2	242·2	161·5
Current density, ampères per sq. foot	3·08	1·24	1·85
Copper deposited in 24 hours . . . lbs.	881·8	551·2	1,984·2
Refined copper per hour and per h.p. lbs.	4·59	4·59	6·87

current is shown by the horizontal arrows. Figs 170 and 171 show the manner in which the baths are coupled up to each other. To each of the longer walls of the bath, a board is secured in which are wooden pins that keep the electrodes at their proper distance apart, so as to prevent short circuiting. The cells are filled with solution almost up to the level of the lower conductor.

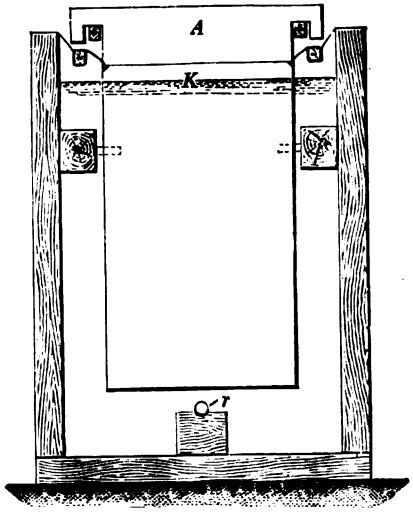


FIG. 169.

The baths themselves are framed of stout plank, strengthened by stout braces on the outside, and lined with lead inside. Their length varies from 3 feet 3 inches to 10 feet or more, according to the number of electrodes. They must possess sufficient depth below the bottom of the electrodes, to prevent the risk of short circuiting between the latter and the slimes thrown down upon the bottom.

The conductors are made of electrolytic copper, and should be an inch or two in thickness. They must be so disposed that any electrode can be immediately removed and replaced by a fresh one.

The anodes are cast in cast-iron moulds; they are provided with short projecting horns at the two upper corners, by means of which they are suspended from the conductors. At Oker they are 3 feet 3 inches long, 1 foot 8 inches wide and 0·6 inch thick. The cathode sheets are made of electrolytic copper and are extremely thin, less

namely than 0·12 inch. In order to be able to remove the deposit of copper from them readily they are painted over with petroleum spirit and their edges coated with paraffin. The cathode sheets are

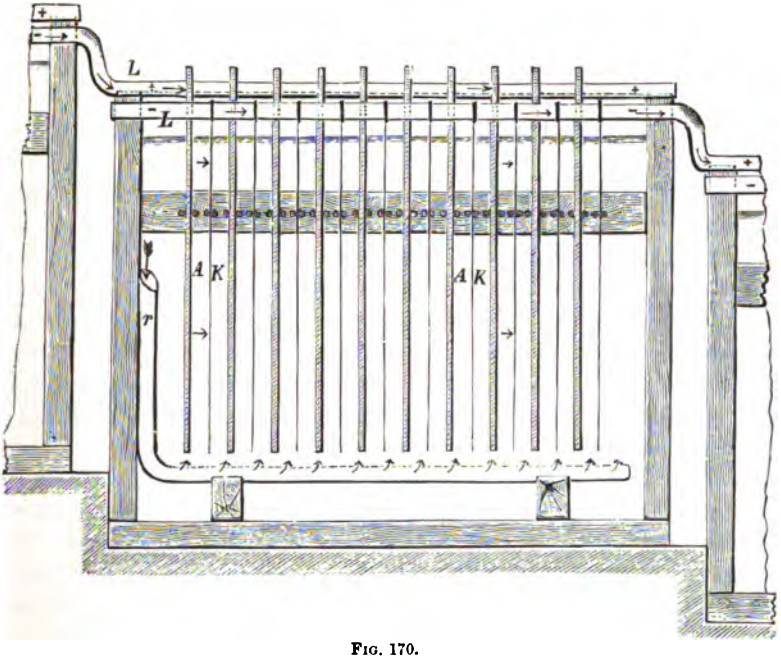
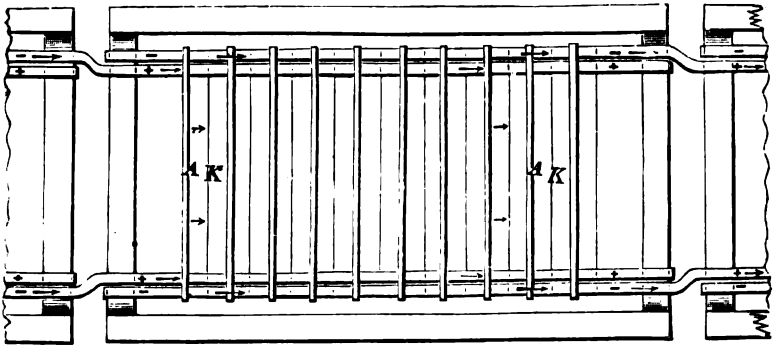


FIG. 170.



Scale $\frac{1}{12}$

FIG. 171.

suspended from the conductors by means of copper strips, 0·8 inch wide and 0·08 inch thick, which may be riveted to the sheets; the junctions must be above the level of the solution or be protected from its action by a coating of paraffin.

Experience has shown that the electrodes are best placed 2 inches apart.

Quite recently, by suitably purifying the electrolyte, it has been found possible to work successfully with high current densities (10 to 20 ampères per square foot); this purification of the electrolyte is performed by means of compressed air, which throws down iron and arsenic in the form of arseniate of iron. By means of an arrangement devised by the brothers C. and H. Borchers of Goslar, the precipitation is carried on so quietly that the solution remains perfectly clear. This device, which besides admitting of the use of high current densities, also produces an excellent circulation of the solution, consists of a leaden tube that reaches from the surface of the solution in each bath down to nearly the bottom. A glass tube drawn out to a fine point dips about half an inch into the solution in each leaden tube, compressed air being forced through the glass tube. The air splits into minute bubbles and is suspended as such in the solution, with the result that the specific gravity of the latter is so far diminished as to rise up in the tube and overflow over its upper edge into the solution in the bath, its place being taken by solution that enters the tube through its lower extremity. A continuous movement of the solution in every bath is thus obtained. The baths are filled from one single set of pipes and emptied out periodically, the latter operation being performed whenever indicated by the condition of the solution. When the bath has become saturated with bismuth and antimony compounds, owing to the presence of these elements in the copper, the electrolyte has to be removed from the baths, and heated air passed through it whilst oxide of copper or basic salts of copper are added to it. It is then filtered, brought up to the requisite strength, acidulated with sulphuric acid and is then again ready to be returned to the baths.

By the employment of this process, a current of 10 ampères per square foot can be applied, so that with the same number of baths, three times as much copper can be treated as by the old process.

The process of Fohster also employs a current of 15 to 20 ampères per square foot. The anodes are suspended as in the Moebius process for parting gold and silver (*i.e.* a number of narrow plates connected by hooks with a metallic rail); the electrolyte is heated and a current of air forced through it, in order to remove easily oxidisable substances, whilst to maintain its strength as regards copper, oxide of copper is added to it. The oxide of copper is produced by the action of a hot air blast upon molten matte, which is thus pulverised and oxidised.

In all the processes hitherto considered for parting copper and silver or for refining copper, the electrodes were arranged in parallel. A number of processes have been devised in the United States, notably by Stalmann, Hayden, Smith and Randolph, in which the electrodes are arranged in series. In Stalmann's process separate anode and cathode plates are employed, whilst in the others the plates of coarse copper are both anodes and cathodes. Stalmann's process was employed for some time at Anaconda, but has been replaced there by Fohster's method; a short description of it may nevertheless prove of interest.[1]

The first anode and the last cathode of each bath are suspended separately, whilst the electrodes between them are united to form couples independent of the others. Each of these couples consists of a cathode and an anode, the surfaces of which, that are turned towards each other, are separated by an insulating layer of glass, asbestos or air, whilst the plates are put into electrical connection with their neighbours by means of copper screws or wires. The current enters at the anode suspended by itself, passes through the electrolyte to the first cathode, by means of the conductor to the anode united with it, from this through the electrolyte to the cathode of the second couple, by means of the conductor to the anode of that couple, through the electrolyte to the cathode of the third couple, and so on till it reaches the cathode suspended by itself at the end of the bath. Thence, with baths in series it passes to the anode of the next bath, whilst with baths in parallel, it returns to the negative pole of the dynamo.

This arrangement is represented by Figs. 172 to 178. A A^1 are two wooden boxes, one inside the other, that form the bath; the interspace between them is filled with some material, like asphalt or cement, that is impervious to the electrolyte. C, C^1, C^2, etc. are the anode plates suspended by the projections c, which rest either directly on the sides of the bath or on bars of indiarubber, wood, or some other nonconductor. E, E^1, E^2 are the cathodes of sheet copper which are also suspended in the electrolyte. D is the dynamo. The first anode C of the bath is connected by means of the conductor H with the positive pole of the machine. The first cathode E is electrically connected with the second anode C^1, either by means of copper bolts *e* (Fig. 174) or by means of copper rods and straps F (Fig. 176). The second cathode plate E^1 is similiarly connected with the third anode C^2, and all the following cathodes and anodes are similarly

[1] Patent No. 467,350, dated January 19, 1892, and Patent No. 467,484, dated January 19, 1892.

connected in couples, up to the last cathode, which is separate and which is connected to the negative pole of the dynamo by means of the conductor G. The individual couples of plates are separated from

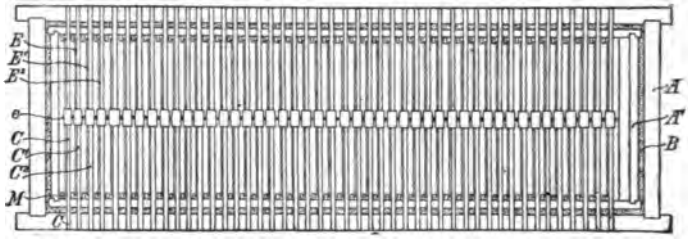


FIG. 172.

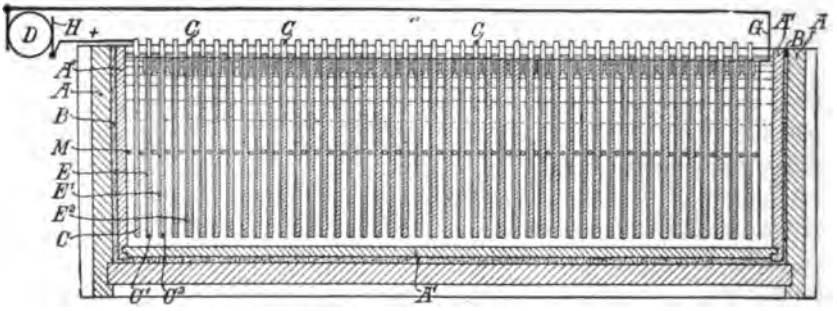


FIG. 173.

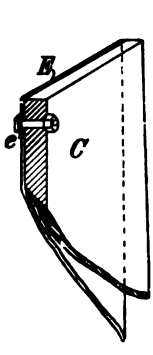


FIG. 174.

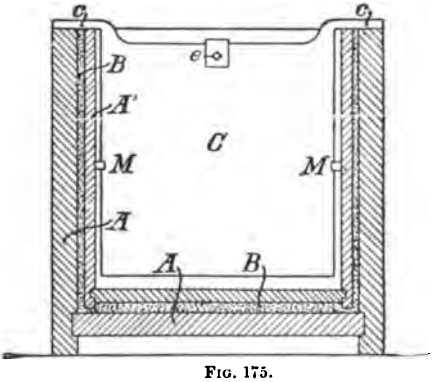


FIG. 175.

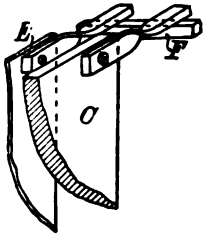


FIG. 176.

each other by means of glass or porcelain studs suitably disposed on and along the inner long sides of the bath.

If several baths are to be employed in series the last cathode of

one is electrically connected with the first anode of the next (Fig. 177), whilst the last cathode of the last bath is in connection with the negative pole of the dynamos. If the baths are to be arranged in parallel (Fig. 178) each bath is separately connected with the positive and negative poles of the dynamo.

With this arrangement the current enters the first anode, passes through the electrolyte to the first cathode, where it deposits copper, sending SO_4 to the anode, then through the conducting fastening to the second, and so on till it reaches the last cathode whence it returns to the negative pole of the dynamo.

In the Hayden, Smith and Randolph processes, all cathodes, except

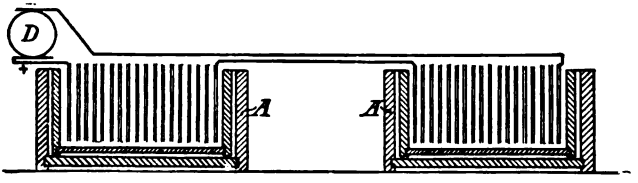


FIG. 177.

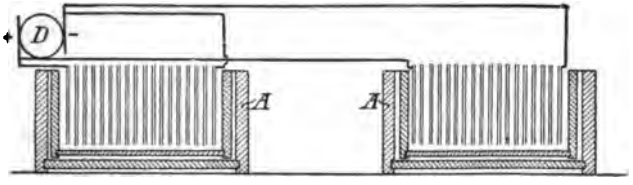


FIG. 178.

the last one of the last bath, are dispensed with, and similarly only the first plate of the first bath can be looked upon as a true anode. As already noted, all the other plates (of coarse copper) act simultaneously as anodes and cathodes; when the circuit is closed and the current passes, the copper is dissolved away from each anode face of each plate and is deposited upon the cathode face of the plate opposite, so that after a certain time each plate will be transformed into electrolytic copper. The current must then be stopped, otherwise this electrolytic copper would in its turn be dissolved and precipitated upon the next opposite plate.

In Hayden's method the electrode plates are suspended vertically, whilst in Smith's and Randolph's methods they lie horizontally In Smith's arrangement the uppermost plate is connected with the

positive, and the lowest plate with the negative pole of the current; the copper therefore travels from above downwards, that is to say it is deposited upon the upper surface of each plate. Linen diaphragms have, therefore, to be inserted between the plates to prevent impurities from dropping down upon the electrolytically deposited copper.

In Randolph's process, the lowest plate is connected with the positive, and the topmost plate with the negative pole of the current, so that the copper travels from below upwards, that is to say the copper is deposited upon the under surface of the plates. The electrolyte is made to circulate horizontally; diaphragms are not required in this arrangement.

Hayden's process has the advantage over those of Smith and Randolph that any interruptions are easily discovered and overcome, whereas in the latter method the electrodes have to be removed from the baths should anything go wrong.

In all these three processes, the plates of coarse copper must be of accurately uniform thickness, otherwise their transformation into electrolytic copper would not be simultaneous; the plates must therefore be submitted to an expensive series of preparatory operations such as rolling, gauging and sorting. But even when the thickness is uniform, certain irregularities in the deposition of the copper are unavoidable, due to want of uniformity in the structure of the coarse copper or to the adherence of impurities to its surface. The advantage of these processes lies in the fact that, when the copper is dissolved rapidly and the plates are not too thick, the stock of copper contained in the baths is comparatively small. At Baltimore, using the Hayden process, plates of coarse copper $\frac{1}{4}$ inch thick are dissolved in 12 days with a current density of 16 amp. per square foot.

These processes have not come into use in Europe, and even in America they appear to have been set aside in favour of those working in parallel.

Figs 179 and 180 show the arrangement of a complete plant for the electrolytic extraction of copper on a scale of about $\frac{1}{200}$.

The baths are arranged stepwise one below the other in two rows, to facilitate the circulation of the solution. The latter flows from the storage tank B through leaden tubes, which project just above the bottom of the topmost tank, and escapes through perforations in the ends of these tubes; from the topmost tanks the solution flows similarly to those immediately below, and so on till it escapes from the lowest tanks into the storage tank B_1, whence it is pumped by the pump P back into the upper storage tank to again traverse the

series of baths. M is the steam engine, driving the dynamo D by means of belting. The path of the electric current from the terminals of the dynamo through the circuit is shown by arrows.

The baths may be placed one close behind the other; sufficient space must however be left between the rows, so that both the longer sides may be readily accessible.

As already stated, the circulation of the solution must be an active one.

The thickness and length of the conductors conveying the current from the terminals of the dynamo to the baths depend on the tension

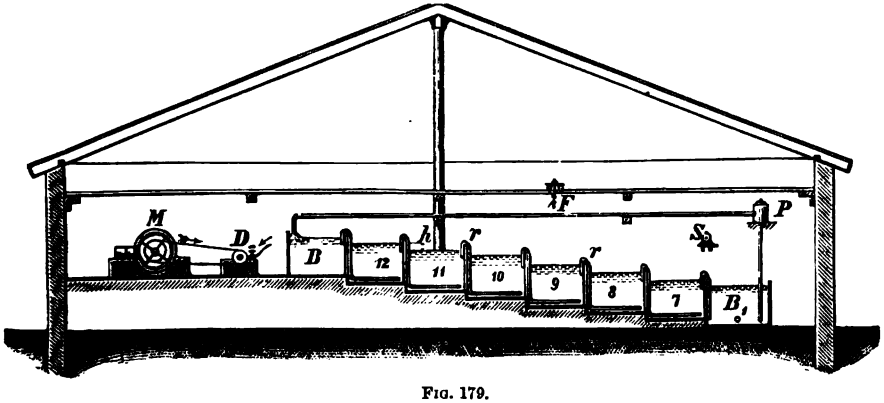


FIG. 179.

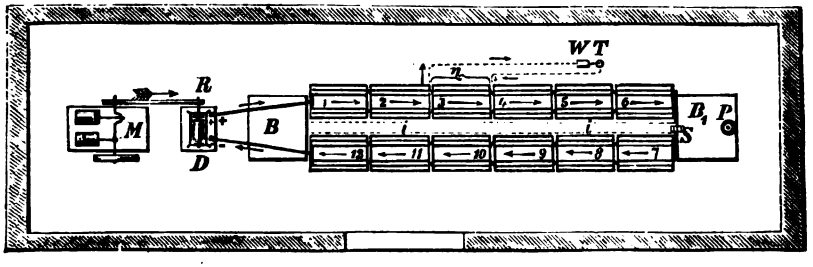


FIG. 180.

and strength of the current as well as on the number of baths. They must be thicker and shorter, the greater the strength of the current. In the better known electrolytic plants, the section of the conductor is such that each square inch carries from 258 to 774 ampères.

The plates of copper deposited at the cathodes are allowed to attain a thickness rather less than that of the anodes.

The electrolytic extraction of copper is open to the objections that

the plant is costly, that the solution of copper at the anodes and its deposition at the cathodes is comparatively slow, so that the copper remains in the baths for a considerable period as dead capital, and that, especially with impure copper, the electrolyte needs frequent renewal. These objections are however in most cases more than counter-balanced by the good quality of the copper produced and the value of the precious metals contained in the anode slimes.

LEAD

Physical Properties

Lead possesses a characteristic bluish-gray colour, and a well-marked metallic lustre. It loses this lustre on exposure to the air, its surface becoming dull gray. It is soft enough to be indented with the nail and can be cut with a knife, the softness of the metal increasing with its purity. Its malleability is such that it can be rolled into thin sheets, and, by previous heating, it can be "squirted" into rods and tubes; it cannot, however, be drawn into fine wire on account of its want of ductility and its low tensile strength. The specific gravity of lead lies between 11·254 and 11·395, and is only very slightly increased by rolling; according to Knab[1] the specific gravity of cast lead is 11·352, of rolled lead 11·358. The specific gravity is lowered by the presence of other metals, so that it furnishes an indication of the softness and purity of the lead.

Lead crystallises in the cubical system, and melts between 334° and 336° C. At a bright red heat, in the presence of air, it volatilises perceptibly, but only to a very slight extent if air be excluded; at a white heat (1600°—1800° C.) it boils.

The conductivity of lead for heat and electricity is low. According to Wiedemann and Franz, taking silver as 100 in each case, the conductivity for heat at 12° C. is 8·5; and for electricity at the same temperature 10·7.

Antimony, arsenic, copper and zinc diminish the softness of lead when present to any considerable extent, antimony and arsenic rendering it brittle, hard, and easily fusible. The presence of antimony is desirable in hard lead (antimonial lead), and alloys containing over 20 per cent. of antimony are used for the production of type metal, metal for bearings, shot and bullets. Lead used for rolling into sheet should, on the contrary, be free from arsenic and antimony.

[1] *Traité de Métallurgie.* Paris, 1891.

Metallic sulphides act similarly to arsenic and antimony in destroying the softness of the metal.

Bismuth in small quantities does not exert any injurious influence on the physical properties of lead. Even when present to a considerable extent it does not appear to interfere with its malleability, as, according to Junge,[1] lead containing 1·92 per cent. of bismuth is as easily rolled into sheets as soft lead quite free from the former metal.

Copper occurs in such small amounts in properly refined lead that it is without influence upon its physical properties, though even this small amount is detrimental in the case of lead which is to be used in making glass, or for the manufacture of white lead, as it imparts a greenish tint to both. According to Hampe, borax glass containing only 0·0009 per cent. of copper oxide is scarcely coloured, whilst the presence of 0·0012 per cent. imparts to it a distinct green tinge.

Iron, zinc, nickel and cobalt only occur in such minute quantities in refined lead that their influence on its physical properties is unimportant.

Chemical Properties

Lead is not altered by dry air, but, exposed to the ordinary atmosphere, it becomes covered with a superficial coating of suboxide, Pb_2O. When melted in air its surface becomes first iridescent, and then covered with a grayish powder or dross (*bleiasche*). At a red heat it is converted into lead monoxide, and after long heating this changes into red lead (Pb_3O_4 or Pb_4O_5). Moderately concentrated nitric acid easily dissolves lead. In large pieces it is only slightly attacked by hydrochloric acid or by cold sulphuric acid of less than 60° B., its surface becoming covered with a layer of chloride or sulphate, which prevents further action; in a state of fine division, however, it is slowly converted into the corresponding salts by these acids. Hot concentrated sulphuric acid attacks it rather rapidly.

Chemical Reactions of Lead Compounds that are of Importance in the Extraction of the Metal

Lead Monoxide (PbO)

Lead monoxide melts at a bright red, but is only volatile at a white heat. It dissolves easily in nitric and acetic acids. Heated with silica to its melting point it forms a freely fluid silicate. It behaves as an acid, towards powerful bases (potash, soda, baryta and lime),

[1] *Jahrbuch für das Berg- und Hüttenwesen im Königreich Sachsen*, 1888, p. 8.

and is dissolved by them. It is produced when lead is heated in air, and, provided that the temperature is kept below the melting point of the oxide, forms a yellow, amorphous powder (massicot); if the temperature be high enough to melt the lead oxide, it forms a transparent, orange-coloured fluid, solidifying to a crystalline red or yellow mass on cooling. In this form, in which it is obtained during the separation of silver from lead, it is known as litharge (*bleiglätte*); it is distinguished, according to its colour, as yellow or silver litharge and red or gold litharge, the two varieties not differing, however, in chemical composition. On heating, yellow litharge becomes red, regaining its colour on cooling, whilst red litharge becomes yellow if quickly cooled after heating.

Large masses of molten litharge, when allowed to cool slowly, fall to pieces, owing to expansion taking place, and form partly fine powder and partly crystalline flakes with metallic lustre. This phenomenon is due to the absorption of oxygen by the molten litharge and the evolution of the gas upon solidification. On long exposure to the air litharge slowly absorbs carbon dioxide.

Heated in contact with carbon or carbon monoxide it is easily reduced to metal. Heated to bright redness with lead sulphide, in the proportion of two molecules of litharge to one of sulphide, the whole of the lead in both compounds is reduced to metal and sulphur dioxide evolved, according to the equation:—

$$PbS + 2PbO = 3Pb + SO_2,$$

any excess of litharge over this amount remaining unreduced. With other metallic oxides, litharge forms easily fusible mixtures, even if the other oxide is not itself fusible. To many metals and metallic sulphides it yields oxygen, an equivalent quantity of lead being set free; antimony, arsenic, tin, bismuth, copper, zinc and iron are thus all more or less completely oxidised. Red lead is a compound of monoxide and peroxide, and has been given the formula Pb_3O_4. It is a bright red powder, obtained by prolonged heating of the amorphous monoxide at a temperature of 300° C.; at higher temperatures it is resolved into oxygen and the monoxide.

LEAD SULPHIDE

It occurs in nature as the mineral galena, and can be artificially prepared by melting together sulphur and lead, or by adding sulphuretted hydrogen to a solution of a lead salt. It is also produced in smelting lead ores, as a sublimate on the cooler parts of the furnace walls.

Lead sulphide melts in the absence of air at a bright red heat, forming a thin liquid, and volatilises at a higher temperature; the molten sulphide easily permeates clay crucibles. According to Fournet, if lead sulphide is heated to redness in a carbon crucible, it loses part of its sulphur and is changed into a mass, the upper part of which is composed of monosulphide PbS, whilst the lower portion consists of subsulphide Pb_2S. This subsulphide can be obtained in the pure state in the form of dull gray scales by melting together lead and lead monosulphide in molecular proportions under a layer of borax glass; according to Bredberg, if the borax cover be omitted, a lower sulphide of the composition Pb_4S is obtained. Percy's researches led him to the conclusion that lead can be melted in all proportions with its sulphide, forming whilst fluid a homogeneous mass, which, however, separates on cooling into two distinct layers of lead and monosulphide.

If lead sulphide be submitted to prolonged heating in the presence of air (roasting), the temperature being kept below its melting point, it is converted into monoxide mixed with a certain amount of sulphate. If the roasting be interrupted at an earlier stage of the process, then a mixture of monoxide, sulphate and sulphide is obtained, the relative proportions of the three compounds depending on the duration of the roasting. Both oxide and sulphate are formed in the roasting of lead sulphide as soon as the temperature reaches a point at which the mass becomes pasty or fluid. As already mentioned, lead oxide reacts with lead sulphide according to the equation :—

$$2PbO + PbS = 3Pb + SO_2.$$

When lead sulphate is heated with the sulphide in equal molecular proportions, sulphur dioxide is evolved, and the lead in both compounds is obtained in the free state :—

$$PbS + PbSO_4 = 2Pb + 2SO_2.$$

If the sulphide is present in excess, then a corresponding amount remains undecomposed, whilst according to some authorities who admit the existence of a subsulphide, this is also formed in addition to lead and sulphur dioxide.[1]

In the first case, supposing the bodies to be present in the proportion of two molecules of sulphide to one of sulphate, then the reaction would be represented thus :—

$$2PbS + PbSO_4 = 2Pb + PbS + 2SO_2,$$

or in the latter case by the equation :—

$$2PbS + PbSO_4 = Pb_2S + Pb + 2SO_2.$$

[1] See also Jenkins and Smith, *Trans. Chem. Soc.*, 1897.

If the sulphate is present in excess, then, according to the quantity present, either metallic lead and monoxide are produced, or the oxide only, as instanced by the following equations, which represent the reactions taking place between one molecule of lead sulphide and two and three molecules of sulphate respectively :—

$$PbS + 2PbSO_4 = 2PbO + Pb + 3SO_2$$
$$PbS + 3PbSO_4 = 4PbO + 4SO_2.$$

Working on the lines indicated by the foregoing reactions, metallic lead can be obtained from the sulphide by first roasting it up to a certain point, and subsequently submitting the roasted mass to a higher temperature.

When lead sulphide is melted together with alkalies or alkaline earths, partial decomposition ensues, metallic lead and alkaline sulphides and sulphates being produced. Sulphide of lead melted with cupric oxide yields cupriferous lead together with a sulphur compound of copper and lead, and a mixture of cuprous and lead oxides. Ferric and ferrous oxides cause no separation of lead from the sulphide.

Melted together with metallic iron, lead sulphide is reduced with the formation of ferrous sulphide. This reaction does not, however, take place in the simple way that the equation :—

$$2PbS + 2Fe = 2FeS + 2Pb$$

seems to indicate, but it depends upon the marked tendency which iron sulphide exhibits to form double sulphides, so that part of the lead sulphide is converted into a double sulphide (*lead matte*).

Instead of the theoretical 86·6 per cent. of lead yielded by the pure sulphide, only 72 to 79 per cent. can be obtained in this way, the remainder existing as lead sulphide combined with iron sulphide in the matte. According to observations made at the smelting works in the Upper Harz, the amount of lead obtainable from the sulphide by means of metallic iron depends both upon the temperature at which the operation is conducted, and upon the relative amounts of iron and lead sulphide present. The higher the temperature the more complete is the decomposition, and the most favourable ratio between the amounts of iron and of sulphide is 20–25 parts of the former to 100 parts of the latter. This is in about equal molecular proportions, and the reaction may then be expressed as follows :—

$$3PbS + 3Fe = 2Pb + (PbS + Fe_2S + FeS).$$

If the iron is present in smaller amounts, then less lead is separated. By increasing the amount of iron more lead is set free, but the

amount so obtained is much smaller than should be produced by the excess of iron employed.

By melting lead sulphide with copper, it is readily, though not completely, reduced. Zinc and tin react only slightly, and antimony not at all. Basic ferrous silicate (subsilicate) in presence of charcoal reduces lead sulphide to metal when heated with it to its melting point :—

$$Fe_4SiO_6 + 2PbS + 2C = Fe_2SiO_4 + 2FeS + 2Pb.$$

LEAD SULPHATE ($PbSO_4$)

It melts at a high temperature, but is only very slightly volatile.

Strongly heated with the requisite amount of carbon it is reduced to sulphide with the formation of carbon dioxide according to the equation :—

$$PbSO_4 + 2C = PbS + 2CO_2.$$

If the carbon is present in smaller proportions a portion of the sulphate remains unaltered, thus :—

$$2PbSO_4 + 2C = PbSO_4 + PbS + 2CO_2$$
$$4PbSO_4 + 2C = 3PbSO_4 + PbS + 2CO_2$$

By heating with lead sulphide, the sulphate is decomposed, as previously described (p. 278). By melting together with silica, it is converted into lead silicate with evolution of sulphur trioxide or of sulphur dioxide and oxygen.

Lead sulphate is dissolved by aqueous solutions of the chlorides of the alkalies as well as by calcium chloride ; from these solutions the lead can be precipitated by means of zinc or iron.

LEAD CARBONATE ($PbCO_3$)

It decomposes on heating to 200° C. into monoxide and carbon dioxide. Heated with carbon or carbon monoxide up to the temperature at which the oxide is reduced, it is converted into the metal.

LEAD SILICATE

According to L. Beck's researches, conducted in Percy's laboratory, all lead silicates are easily fusible down to the trisilicate, $Pb_2Si_3O_8$. The higher silicates are difficultly fusible, and when the proportion between the lead oxide and silica is in the ratio of 1 : 18, only a fritted mass is obtained.

Heated with charcoal, the easily fusible basic silicates yield a portion only of their lead, whilst difficultly fusible acid silicates or mixtures of

free silica and acid silicates remain behind. Heated with the requisite amount of ferric oxide and charcoal the whole of the lead is reduced and a ferrous silicate formed, and by heating a mixture of lead silicate and metallic iron to bright redness, the same result is obtained.

Mixed with lime and charcoal, it is only reduced at high temperatures. A mixture of lime, ferrous silicate and charcoal reduces it at a lower temperature with the formation of calcium-ferrous silicate.

The sulphides of iron, barium and calcium reduce lead silicate to metallic lead at high temperatures, silicates of the metals being formed.

LEAD ANTIMONIATE

is easily reduced by carbon or carbon monoxide forming antimonial lead.

LEAD CHLORIDE

Lead chloride is soluble in a large quantity of cold and more freely in hot water. It is only difficultly soluble in dilute but readily in strong hydrochloric acid. Fused with oxide or sulphide of lead it mixes with them in all proportions, and is completely reduced by carbon monoxide.

LEAD ALLOYS

Lead alloys with tin, gold, silver, bismuth, arsenic and antimony in all proportions. Copper and zinc dissolve it only to a limited extent, and iron in only very small amounts. If a copper-lead alloy be heated up to the melting point of lead the greater part of that metal flows away, leaving behind a more difficultly fusible copper-lead alloy.

From its alloys with gold and silver, lead can be separated as oxide by submitting the alloy to an oxidising fusion. Arsenic, antimony, zinc, iron, nickel, cobalt and tin can be separated from their respective alloys with lead, as arseniate or antimoniate of lead, in the first two cases, or as oxides in the case of the remaining metals by melting the alloy in an oxidising atmosphere.

If a lead-silver or a lead-gold alloy be made the anode in an electrical circuit, a lead plate serving as cathode and a solution of a lead salt (acetate) as the electrolyte, then on passing a sufficiently powerful current, the lead of the alloy is deposited on the cathode, whilst the precious metal remains behind at the anode in the form of a fine mud.

Ores of Lead

GALENA (PbS)

The most important ore of lead is lead glance or galena, containing 86·57 per cent. of lead and 13·43 per cent. of sulphur. It usually

contains silver either as an isomorphous mixture of silver sulphide or as finely disseminated silver ores.

The silver content varies between the merest trace, and one per cent., usually lying between 0·01 and 0·1 per cent. (galena from Mechernich, in Rhenish Prussia, contains from 0·01 to 0·014 per cent., that from the veins of the Upper Harz up to 0·1 per cent.). Fine grained galena is usually richer in silver than the coarse, and especially than the scaly varieties, though at Broken Hill, N.S.W., exactly the reverse is the case.

Galena is found in nearly all countries. In Europe, in Germany (Upper and Lower Harz, the Erzgebirge, Upper Silesia, Mechernich in Rhenish Prussia, Stolberg, Bensberg, Ramsbeck in Westphalia, Siegen, Holzappel in Hesse-Nassau, Ems, Braubach); in Austro-Hungary (Carinthia, Hungary, Transylvania, the Tyrol and Bohemia); in Great Britain (Shropshire, Devonshire, Cornwall, Wales, the Isle of Man, and in parts of Scotland and Ireland); in France (Pontgibaud); in Belgium (Bleiberg near Mons, Corphalie); in Russia (Allagir); in Spain (Carthagena, Linares, Andalucia, St. Sebastian, Badajoz); in Italy (Sardinia); in Greece (Laurium), as well as in Sweden and Norway and Turkey. In America it occurs in the United States, in Mexico and Brazil. The most important American deposits are found in the States of New York, Illinois, Wisconsin, Iowa, Colorado (Leadville), Missouri, Idaho, Montana, Utah, Nevada, California and New Mexico. In Africa, galena occurs in Tunis and Algeria (Kefoun and Teboul); in Asia in the Altai Mountains and in India (the kingdom of Ava, Lao Mountains and Malla-Malla Mountains); in Australia, in New South Wales (Broken Hill), in Queensland and in Tasmania.

Galena is accompanied mainly by zinc blende, iron and copper pyrites, arsenical and antimonial compounds, as well as by quartz, calcspar, dolomite and spathic iron ore.

CERUSSITE ($PbCO_3$)

contains 77·52 per cent. of lead. This is a decomposition product of galena, and consequently usually occurs in the upper portions of plumbiferous deposits. In the earthy state, mixed with clay, it is known as "lead earth." Sometimes it occurs mixed with so much carbonaceous matter as to be quite black in appearance, and is then known as black lead ore (*schwarzbleierz*). In some cases it is argentiferous owing to an admixture of the chloride or iodide or of native silver, (Leadville, Colorado, United States; Broken Hill, N.S.W.). Cerussite does not often occur in sufficiently large amounts to enable it to be separately smelted. The most important localities are in the moun-

tain districts of Carthagena and Linares (Spain), in the Laurium Mountains (Greece), in the Altai Mountains (Asiatic Russia), and especially at Leadville (Colorado), as well as recently at Broken Hill, N.S.W.

LEAD SULPHATE, ANGLESITE ($PbSO_4$)

with 68·3 per cent. of lead is also formed by the decomposition of galena, and is usually found on the outcrop of ore deposits, but to a much smaller extent than the carbonate, so that it is only exceptionally mined by itself. It is poor in silver, and has been obtained in considerable quantities in France, Spain, Sardinia and Australia.

PYROMORPHITE

$$PbCl_2 + 3(Pb_3P_2O_8)$$

with 69·5 per cent. of lead and *Mimetesite*, $PbCl_2 + 3(Pb_3As_2O_8)$, are also formed by the decomposition of galena, and occur in the upper portions of deposits of lead ores. Both substances contain only traces of silver, and neither occur in sufficiently large amounts to be separately smelted. They occur at Ems (Hesse-Nassau, Prussia) and St. Martin (Spain).

The remaining lead-containing minerals are seldom used for the production of the metal. Amongst others are Wulfenite (lead molybdate), Crocoite (lead chromate), Stolzite (lead tungstate), Vanadinite (lead vanadate and chloride), Mendipite (an oxychloride), Boulangerite ($3PbS,Sb_2S_3$), Bournonite and Jamesonite.

PLUMBIFEROUS METALLURGICAL PRODUCTS

In addition to the ores of lead a variety of substances, obtained in the various processes of lead smelting, and especially in the extraction of silver, are also employed as sources of the metal. They chiefly consist of oxides, silicates, antimoniates, sulphides and alloys of lead. The oxidised products are litharge, cupellation hearths, lead dross and silicates; there are also the various lead slags, furnace scums and residues, mattes and alloys containing lead, zinc scum from Parkes's process and plumbiferous black copper.

The Production of Metallic Lead

The extraction of lead from its ores and from plumbiferous smelting residues is mainly effected by dry methods. Wet methods are not employed for the extraction of the metal from its ores on account of the much easier application of dry processes, and they are only very exceptionally resorted to in the treatment of plumbiferous

residues (dissolving lead sulphate from burnt pyrites by means of calcium chloride solution and precipitating the lead by metallic iron). Electrolytic processes are not employed in the treatment of ores, nor have they made much progress in the treatment of silver-lead alloys as the dry methods are less costly. Lead obtained by dry processes from ores or plumbiferous materials is usually contaminated with other metals which act disadvantageously upon it, and it has, therefore, to be submitted to a process of purification, the so-called *softening* or *improving*.

EXTRACTION OF LEAD FROM ITS ORES

The chief ore of lead is galena. Next in importance comes the carbonate, which is, however, only comparatively rarely smelted by itself, and still more exceptional is the treatment of sulphate ores alone.

THE EXTRACTION OF LEAD FROM GALENA

A consideration of the various chemical relationships of lead sulphide and of its reactions with other compounds which have previously been considered will show how it is possible to obtain metallic lead from it in several ways. Three smelting processes are in use:—

1. The galena is first roasted to such a degree that a mixture of lead sulphide, oxide and sulphate is produced containing the three compounds in definite proportions, and then the temperature is increased, whereupon the oxide and sulphate react with the remaining sulphide, producing metallic lead and sulphur dioxide.

2. The roasting of the galena is first carried out until it is entirely decomposed or is practically converted into lead oxide mixed with a small amount of sulphate; this is then reduced by heating it with carbon. The sulphate present is either converted into silicate by melting with silica at the conclusion of the roasting operation, and this silicate is reduced to metal in the subsequent smelting with carbon and oxide of iron, or else it is reconverted in the latter operation into sulphide, which in its turn is reduced by metallic iron.

3. Galena is decomposed by being heated with metallic iron, lead being set free, and a compound of sulphide of iron and sulphide of lead (lead matte) produced.

The first of these methods is known as the air-reduction process ("*Röstreactionsarbeit*"), the second as the roasting and carbon reduction process ("*Röstreductionsarbeit*"), and the third as the precipitation or iron-reduction process ("*Niederschlagsarbeit*"). In all these processes

the bulk of the silver in the ores finds its way into the lead produced which is known as *work-lead* (*"werkblei"*). In many cases these processes are not kept distinct, but are to a certain extent combined, as for instance when residues from the first process are reduced with carbon or with metallic iron, or the second method may be partially carried out and the product then worked up by either of the other two methods.

The air-reduction processes are conducted in reverberatory furnaces or hearths. In the roasting and carbon-reduction process, that part of the operation that involves roasting is carried out in one of the various forms of calcining furnace, and the reduction in blast furnaces, whilst the iron-reduction process is conducted in blast furnaces, or occasionally in reverberatory furnaces.

The selection of the process most suitable for a particular ore depends upon the substances which are associated with the galena, as well as upon the character of the available fuel. The air-reduction process admits of the use of raw fuel, but demands a rich and pure galena, large quantities of foreign substances interfering with the reaction between the sulphide and the oxide and sulphate. The presence of quartz or acid silicates precludes the employment of this method, comparatively small amounts hindering the reactions, owing to the formation of lead silicate.

The iron-reduction process requires a carbonised fuel, highly ferruginous fluxes from which iron can be reduced in the blast furnace, and a galena which is rich in lead, and contains only small quantities of other sulphides (particularly pyrites, stibnite and zinc blende), as these are reduced to a certain extent by the iron, involving a waste of that material, whilst a portion of the reduced metal alloys with the lead. The presence of quartz or earthy matter is not disadvantageous. As galena is only reduced by iron at a high temperature, a large amount of carbonised fuel is required in the conduct of this process. The presence of lead in the resulting matte also renders necessary a subsequent treatment of this product. If the ore contains copper, even if present in only small amounts, it is found in the matte, and can be recovered from it together with any silver that may be present. The advantages of this process are, that no roasting of the ore is needed, and consequently there is a proportionately smaller loss of silver by volatilisation; the yield of lead is large, and it is possible to obtain any copper the ores may contain, even if only present in small amounts. Nevertheless, in most instances these are counterbalanced by the above-named disadvantages, especially by the large consumption of fuel,

and by the comparatively slow rate of decomposition of the galena, and the large expenditure in wages.

The iron-reduction process is therefore rarely carried out as a complete process by itself, but only where exceptional conditions prevail (as in the Upper Harz), it being usually combined with the roasting and carbon-reduction process. This latter process (*röstreductionsarbeit*) is available for all classes of ores without regard to any admixtures they may contain, and their percentage of lead may be lower than is the case with ores to be employed for either of the other processes. Copper if not present in too small a quantity can also be collected in the matte if the formation of the latter is promoted by roasting the ore less completely. This method is the one chiefly employed.

If local conditions permit, if the ore is a pure and rich one free from quartz or acid silicates, and raw fuel is cheap, then the air-reduction process (*röstreactionsarbeit*) would be indicated; all other ores would be treated by the roasting and carbon-reduction process, or this combined with the iron-reduction method. The latter method would only be employed by itself under exceptional conditions; as, for instance, if a lead ore were available containing silver together with a small amount of copper, enough, nevertheless, to make its recovery worth while, and if labour could be procured cheaply.

THE AIR-REDUCTION PROCESS (*Röstreactionsarbeit*)

The essential feature of this process consists in roasting the galena in air to about 500° C. for such a time that the amount of lead oxide and sulphate formed bears the requisite ratio to the amount of sulphide remaining undecomposed, the reduction being then brought about by heating the mass to a higher temperature. The interaction of the sulphate and oxide is only satisfactorily effected when they are in the pasty state; if they are rendered entirely fluid the reaction is incomplete. It is not, however, possible to carry the roasting of the sulphide to the point at which the exact quantity of oxide and sulphate requisite for the reduction of the whole of the lead is produced, and, as during the period of the reaction more oxide and sulphate are produced, these are usually present in excess. This excess, together with some sulphide which escapes decomposition, becomes mixed with the gangue, and together constitute a residue rich in lead needing special treatment for its recovery. In the case of pure lead ores which only leave a small residue, consisting essentially of sulphate and oxide, this residue, when small charges are worked, can be treated direct by heating

with coal and much of its lead reduced. By crushing and washing, the lead can be separated from what residue remains, and the residue can be worked over again with a fresh charge of ore. As, however, the liberation of the lead from the residue in this way requires a high temperature accompanied by a considerable loss of lead by volatilisation, it is preferable to leave a proportionately large quantity of the metal in it, and to afterwards treat it in the blast furnace or slag-hearth.

The air-reduction process is, therefore, always combined with other methods for recovering lead from the residues produced by it.

The air-reduction process can only be profitably employed in the case of ores consisting of tolerably pure galena. Ores containing less than 60 per cent. of lead, even if the associated gangue is such as not to exert any injurious influence on the process, cannot be employed. The ores in general use contain not less than 70 per cent. of metallic lead.

An admixture of 4 to 5 per cent. of quartz or a corresponding amount of an acid silicate with the ore, renders the process unprofitable owing to the formation of lead silicate. This body not only will not react with lead sulphide, oxide or sulphate, but in consequence of its low melting point, it fuses and coats these substances so as to prevent their interaction. The presence of the alkaline earths (lime, magnesia, baryta), in not too large amounts, is advantageous, as they assist in keeping the mass in the requisite pasty state during the last or reaction stage of the process, and in many cases lime is added to the ore for this purpose. If present in large proportion (12 per cent. and over), it prevents the various lead compounds from coming into contact, and consequently decreases the yield of lead.

Spathic iron ores in the presence of silica give rise to very fluid slags, and are, therefore, to be avoided.

Sulphides of other metals, which during the period of roasting are converted into oxides, are advantageous, as they not only stiffen the mass but promote the formation of lead sulphate by the action of the oxides of sulphur given off during their decomposition. In large amounts (over 10 or 12 per cent.) they act injuriously, the oxides produced unduly thickening the mass and causing a loss of the entangled lead. A portion of the metallic sulphide would also combine with a part of the galena, giving rise to a matte from which the lead would have to be recovered. Pyrites, zinc blende and copper pyrites act in this way. Copper pyrites also yields some copper to the lead, as the sulphide and the oxide formed in roasting

undergo double decomposition during the period of the reaction, forming metallic copper and sulphur dioxide.

Antimony sulphide, on account of its easy fusibility, causes an undesirable sintering together of the mass, and also produces antimonial lead. Owing, also, to the volatility of the antimony compounds, a portion of lead is lost through this cause. On heating the mass with coal in the extraction of lead from the residue, antimony becomes alloyed with the lead, and the same thing occurs when the residue is worked up in blast furnaces.

Arsenic compounds (mispickel, arsenical pyrites) lose a part of their arsenic by volatilisation, whilst the remainder gives rise to the formation of a speiss. During the operations just mentioned, arsenic is carried into the lead similarly to antimony.

Any silver present in the ores will be found in the lead produced, and nearly the whole of it will be contained in the first portions of the lead. Gold behaves similarly to silver.

The presence of carbonate or sulphate of lead in the ore, in addition to the galena, is very advantageous, as they shorten the roasting period.

In general the air-reduction process is carried out in reverberatory furnaces or hearths, and the working up of the residues in blast furnaces.

When the process is conducted in reverberatory furnaces, the reduction period follows immediately after the process of roasting, whilst in hearths the two reactions are taking place simultaneously, and some lead oxide is reduced by the coal on the hearth. The employment of reverberatory furnaces is more conducive to the health of the workmen, as they are less exposed to the lead fume than in the working of the hearths. The latter are consequently only rarely employed, and under special local conditions. As volatilisation of the lead and the carrying over of part of the ore into the flue during the air-reduction process cannot be avoided, some arrangement for collecting the fume and dust containing lead must be provided.[1]

THE AIR-REDUCTION PROCESS IN REVERBERATORY FURNACES

This process is in practice carried out in different ways and in furnaces of varying construction, according to whether the object in view is a rapid output of lead without regard to loss, or a slower production, accompanied by the smallest possible loss, producing in the one case residues rich in lead, and in the other residues contain-

[1] Schnabel, *Allgemeine Hüttenkunde*, p. 499.

ing a small percentage of metal. These processes may be divided into three classes, known as the Carinthian, the English, and the Tarnowitz or Silesian processes. Formerly a fourth, or French process, was in use for the working of ores, containing as much as 6 per cent. of silica, but this has now been abandoned.

The Carinthian process proper (the process as worked elsewhere has undergone modification) has for its object the production from pure ores, of a very high percentage of the lead contained in them in a pure state. It is carried out with small charges in small furnaces, the process being conducted slowly and so arranged that, for every molecule of lead sulphide present, as nearly as possible one molecule of sulphate and two molecules of oxide shall be formed, the reaction proceeding according to the equations:—

$$PbS + PbSO_4 = 2Pb + 2SO_2$$
$$PbS + 2PbO = 3Pb + SO_2.$$

The recovery of lead from the residue is effected by the addition of coal in the same furnace at the end of the period of reduction.

The process involves a large expenditure for both fuel and labour.

The English process aims at producing a large amount of lead in a short time with a small outlay for fuel. It is accordingly conducted in large furnaces, working quickly at a high temperature, and in such a way that the period of reduction begins when only one molecule of lead sulphate is present for every two molecules of lead sulphide in the charge. According to some metallurgists a subsulphide is formed during the reaction in addition to the lead, and this decomposes into lead and monosulphide when the temperature is lowered. The reaction would consequently be represented by these equations:—

$$2PbS + PbSO_4 = Pb + Pb_2S + 2SO_2$$
$$Pb_2S = Pb + PbS.$$

As the existence of a subsulphide has not been firmly established, the reaction may also be represented as follows:—

$$2PbS + PbSO_4 = 2Pb + PbS + 2SO_2,$$

When the reaction resembles the Carinthian one, the recovery of lead from the residues is conducted in small blast furnaces (slag-hearths). Considerable loss of lead by volatilisation takes place in the English process owing to the high temperature employed.

The Tarnowitz process has for its object a large output of metal, as in the English process, with the employment of a small proportion of fuel and a reduction of the losses of metal to a minimum. It is

accordingly carried out in large furnaces at the lowest possible temperature. As a consequence of this latter condition the amount of lead remaining behind in the residues is great.

The chemical reactions, with the exception of those attendant on the working up of the residues which is done in blast furnaces, are the same as in the Carinthian process.

This process is preferable to the others on account of the smaller loss of lead as compared with the English process, and the larger charges used and consequent smaller expenditure for labour as compared with the Carinthian process.

The French process formerly employed aimed at obtaining most of the lead from ores containing up to 6 per cent. of silica in reverberatory furnaces. The ores were heated at a very low temperature for a long period, so that a large excess of sulphate of lead was obtained in proportion to the undecomposed sulphide. In addition to the production of lead according to the reactions given under the Carinthian process, lead oxide was also formed, thus:—

$$PbS + 3PbSO_4 = 4PbO + 4SO_2.$$

By mixing the residue with coal and reheating after the reaction, the lead oxide was reduced to metal, and a part of the remaining sulphate to sulphide.

On account of the attendant losses of lead and the length of time necessary for the process it has been entirely superseded by the other air-reduction processes.

THE CARINTHIAN PROCESS

In its simple form it is carried out at Bleiberg and Raibl in Carinthia, and with some alterations it has been employed in Belgium, France, Switzerland and the United States of North America, but is now no longer used, partly in consequence of the exhaustion of the ore deposits (as at Engis in Belgium and Davos in the Engadine), and partly in consequence of the introduction of other processes, as in Missouri.

THE CARINTHIAN PROCESS AS CONDUCTED AT BLEIBERG

At Bleiberg the raw material is a calcareous galena poor in silver, in the form of concentrates, and containing from 60 to 75 per cent. of lead.

The arrangement of the furnace in which the process is conducted is shown in Figs. 181–184; *a* is the sloping heating chamber, narrowed at the front end. The hearth has the form of a shallow inclined basin narrowing at the lower end, and is composed of a mixture of clay, poor slag and similar waste, or of old hearths broken into

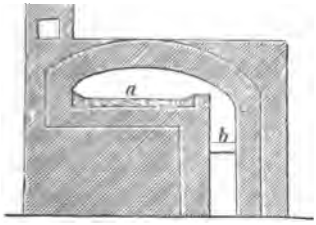


FIG. 181.

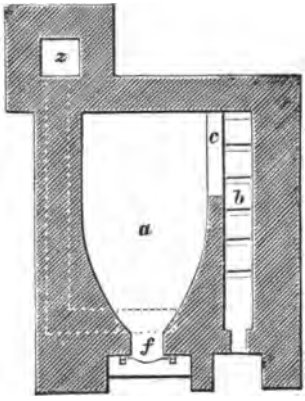


FIG. 182.

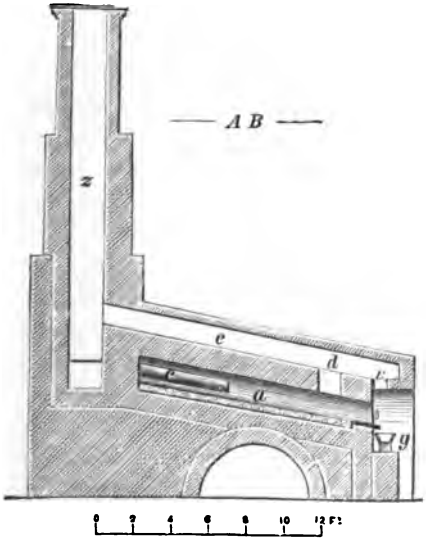


FIG. 183.

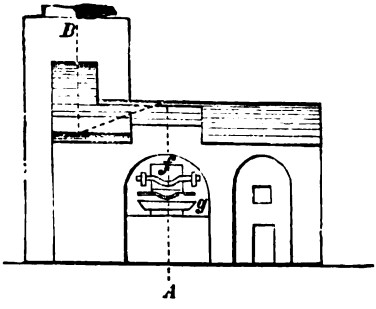


FIG. 184.

small pieces, and the whole fritted together. It is 6 inches thick, 11 feet 6 inches long, 5 feet broad at the upper and 1 foot broad at the lower end. The hearth is inclined at an angle of 9½° in order that the lead may flow down, whilst the solid or pasty residues remain behind. At the lower end of the hearth is the one working door *f*. Below this is a spout through which the separated lead flows from the furnace into a heated cast-iron pan *g*;

it is through this working door that the charge is introduced, the residues withdrawn, and the charge stirred during the process.

The fireplace is placed parallel to the longer axis of the furnace. The grate *b*, if wood is used as fuel as in the present instance, is constructed of stonework, the so-called girdle grate (*gurtenrost*), whilst if lignite is burnt, as is also done in Carinthia, iron bars are used. The fire bridge and the space for the passage of the flame *c* are at the further end of the fireplace and are only 3 feet 6 inches in length. The air necessary for combustion as well as that required for the oxidation of the charge enters through the holes in the grate. As a consequence of this the air passing over the hearth is rarefied and diluted with combustion products, and the roasting proceeds but slowly. The flue *d* is at the front part of the working chamber and communicates by means of the inclined channel *e* with the stack *z*; the flames thus pass over the hearth from back to front. The lead fume escaping from the furnace is led back through the opening *v* into the flue *e*, and so into the stack.

The process is divided into three stages, (1) roasting, (2) rabbling (*rührperiode*), and (3), slag-reduction (*Pressperiode*). In the first stage the partial oxidation of the galena is brought about, in the second the reaction between oxide, sulphate and sulphide occurs, and in the last stage lead is reduced from the residues by means of carbon.

The actual working is conducted as follows:—The charge, which usually weighs from $3\frac{1}{2}$ to 4 cwt., is introduced through the working door into the furnace, previously heated to dull redness, and is spread on the hearth so as to form a layer one to one and a half inches in thickness.

During the first or roasting stage, firing is conducted very gently so as not to fuse the ore. As soon as the mass becomes hot (after about one hour) it is raked and stirred about from time to time. After the roasting has gone on for about three hours, reckoning from the beginning of the whole operation, it is usually far enough advanced to have formed the requisite amount of oxide and sulphate in proportion to the unaltered sulphide (one molecule of sulphate and two of oxide to every molecule of lead sulphide). The exact point is ascertained by the disappearance of the sulphur flame, by the trickling away of some lead from the mass, as well as by the gritty feel which the roasted mass has under the tool.

The second stage, in which the reaction between oxide, sulphate and unaltered sulphide occurs, now begins. The temperature is increased so that the charge becomes pasty and it is well stirred

so as to effect a thorough intermingling of the whole mass. The following reactions take place:—

$$PbS + PbSO_4 = 2Pb + 2SO_2$$
$$PbS + 2PbO = 3Pb + SO_2$$

and the lead set free flows out of the furnace into the iron pan placed at the front to receive it. The separation of the lead ceases after from 3½ to 5 hours' rabbling, and this ends the second stage. At this period about half the total lead in the charge will have been obtained as metal, the remainder being contained as oxide and sulphate in the residue left in the furnace.

This residue is worked up at once in order to obtain as much as possible of the lead contained in it. This constitutes the last or slag-reduction (*bleipressen*) stage, and is effected by taking pieces of coal, or logs of wood, from the grate and mixing them with the mass in the furnace, at the same time raising the temperature. The lead oxide is reduced to metal, and a portion of the sulphate is partially reduced to sulphide, thus:—

$$PbSO_4 + 2C = PbS + 2CO_2$$

The sulphide thus formed reacts with the remaining sulphate, forming lead and sulphur dioxide.

This slag-reduction stage lasts 4 hours and is finished when no more lead runs out from the furnace. In order to save fuel it is usual to work up the residues from two charges together. In this case, as soon as the rabbling of the first charge is finished, the residue is raked out of the furnace and the next charge inserted; when the rabbling of this is finished, the residue from the first operation is put back and the two residues worked together, the operation now taking 7 to 8 hours.

The lead obtained during the slag-reduction stage ("*Pressblei*") is less pure than the lead formed in the rabbling period, because the oxides of other metals such as antimony and copper are reduced at the higher temperature prevailing, and the reduced metals contaminate the lead. This impure lead is submitted to a process of liquation at the lower end of the furnace.

The residue left in the furnace after the slag-reduction period still contains, according to the nature of the ore, from 3 to 9 per cent. of lead. This is concentrated by crushing, sieving and washing, until it contains from 50 to 60 per cent. of lead, and it is then either added in small quantities to the ordinary ore charges or is treated by itself omitting the first and second stages.

In the slag-reduction period considerable amounts of lead are lost by volatilisation, and the consumption of fuel is twice as great as in the rabbling stage. It is consequently preferable not to attempt to extract the lead completely from the residues, but to submit them to an after-treatment in the blast furnace. The loss of lead in the process is variously stated as being between 5 and 14 per cent.; including the lead recovered from the residues, the loss may be taken as between 6 and 9 per cent.

The amount of fuel necessary in the case of ore containing from 64 to 70 per cent. of lead is said to be from 11 to 12 cubic feet of wood for every cwt. of ore. One smelter and one assistant are required for each furnace.

The Carinthian process is one which cannot be recommended for several reasons. The charges worked are small (4 cwt. in 12 hours), and the expenditure in wages is high; during the slag-reduction period the consumption of fuel is great and there is a heavy loss of lead during that stage. It seems likely that its employment even in Carinthia will in time be discontinued. In most other places where it is carried on much larger charges are used and the extraction of lead from the residues is much less thorough.

At Engis in Belgium the Carinthian process was formerly worked,[1] but with some modifications, much larger charges being used, and a larger quantity of lead allowed to remain in the residue, which was afterwards smelted in blast furnaces. The furnace also differed from the ordinary Carinthian furnace as regards the position of the grate, the number of working doors, and the method of admitting the air required during the roasting. The grate was placed at the shorter side of the furnace, and not in the direction of its length. In addition to the working door at the narrow end of the hearth, as in the ordinary Carinthian furnace, there was another opening in one of the longer sides of the furnace, and the air necessary for oxidation was admitted through this opening instead of through the spaces between the grate bars. The inclined hearth was 6 feet 6 inches long, 4 feet broad at the fire bridge, narrowing down to 2 feet 3 inches at the other end. The hearth was composed of a mixture of two parts of clay and one part of coke-breeze fritted together with a certain amount of ore. Ordinary coal was used as fuel.

The ore smelted was a mixture of 93·56 per cent. of galena, 3·74 per cent. of zinc blende, 2·31 per cent. of pyrites, and 0·35 per cent. of calcite. Each charge weighed 12½ cwt. The process differed

[1] Bouhy, *Annales des Mines*, 1870, xvii. p. 159.

from the Carinthian in that the extraction of the lead in the slag-reduction stage was not carried out as completely, from 17 to 20 per cent. of lead having been left in the residue, which was afterwards smelted in blast furnaces with tap cinder. The residue thus worked up formed about 12 per cent. of the weight of the initial charge.

Each charge required 12 hours to work off with one furnaceman and one assistant. For the charge of $12\frac{1}{2}$ cwt, 1·1 tons of coal were used. The loss of lead after working up the residues amounted to 3·93 per cent.

In America (Missouri) the galena from the Mississippi valley, containing from 70 to 84 per cent. of lead, was formerly smelted by

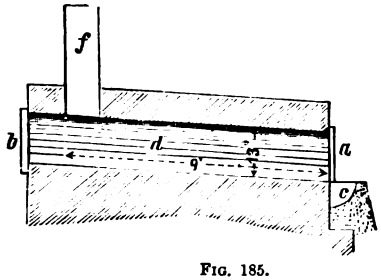


FIG. 185.

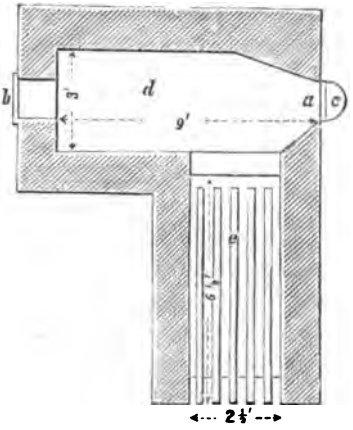


FIG. 186.

the Carinthian process, using, however, larger charges and omitting the slag-reduction stage.[1]

The furnace employed is shown in the Figures 185 and 186, dimensions being given in feet and inches. The working chamber had two doors—*a* and *b*—the ore being charged in through *b*, whilst the lead flowed from the furnace through the hole at the bottom of *a* into pot *c*, and the residue was also removed through this door. The working of the charge was effected through the opening *b*. The grate lay with its length at right angles to the longer axis of the hearth, which was composed of melted up ore residues, and was supported on a cast-iron plate.[2]

[1] Williams, *Geol. Survey of Missouri*, Industrial Report, 1877, pp. 8–101.
[2] Broadhead, *Geol. Survey of Missouri*, 1874, p. 492.

The charge consisted of 14 to 16 cwt. of ore, in pieces varying in size from that of peas to hazel nuts. The roasting stage occupied only an hour and a half, the reaction period (rabbling stage) extending over 7 hours. The residue was then drawn out of the furnace, the slag-reduction stage being omitted. From 9 to 11 hours were occupied in working each charge, which required the labour of a smelter and one assistant, and consumed one and a half cords of wood. No mention is made of the extent of the loss of lead, and the process is now superseded by the air-reduction process conducted in hearths.

THE ENGLISH PROCESS

The characteristic features of this process are as follows. Large charges of galena are subjected to comparatively rapid roasting at a high temperature, not, however, sufficient to render the mass pasty, and then the reaction between sulphate and sulphide is allowed to begin, when the former is present in the proportion of only one molecule to two molecules of unaltered sulphide, thus:—

$$2PbS + PbSO_4 = 2Pb + PbS + SO_2.$$

After this reaction is complete, the cycle of operations is repeated with the residue in the furnace. It is cooled and air freely admitted, so as to produce a further quantity of sulphate, and then on shutting off the air supply and raising the temperature, the reduction again takes place. If necessary the operation is repeated as long as any lead is obtained from the residue. The temperature in the reaction period is, as a rule, so regulated that the mass only becomes pasty; if it becomes unduly fluid, it is stiffened and cooled by mixing slaked lime with it. In the case of ores which contain large percentages of heavy spar, an addition of fluor spar is made with the object of producing a readily-fusible slag, poor in lead, which can easily be separated from the residue. Ores which contain fluor spar yield a fluid slag without other addition. A considerable quantity of residue is left in this process, consisting chiefly of lead sulphate and oxide, together with the gangue of the ore. With the view of avoiding excessive losses of lead a large amount (up to 50 per cent.) is allowed to remain in the residue, which is worked up in small blast furnaces.

The Cornish process of smelting cupriferous lead ores is a modification of the English one, being a combination of the air-reduction and the iron-reduction processes. The ores are first roasted in a special reverberatory furnace, and the roasted material is subse-

quently treated in a reverberatory melting furnace (*flowing furnace*). In the latter the reaction between oxide, sulphate and sulphide is effected, and the lead still remaining in the residue is obtained partly by the reducing action of coal which is added to it, and eventually by the action of metallic iron on the remaining lead sulphide. Most of the lead in the ore is obtained in the metallic state, but a part of it, together with most of the copper, goes to form a regulus or matte, from which the lead is recovered by the roasting- and carbon-reduction process. The furnace in which the English process is conducted has in its interior a sump or well for the purpose of collecting the lead produced. This is situated at the front of the furnace, usually near the flue or occasionally nearer to the centre, and is connected by a tap-hole with a vessel placed in front outside the furnace.

The hearth is rectangular or trapezoidal, sloping in all directions towards the sump, the slope in the Flintshire furnace being a steep one. In England the bed is usually composed of residues or *gray slags*, or of a mixture of clay and slag. At the back and front of the furnace are working doors, up to the number of three on each side. The lead which collects in the well is allowed to flow from time to time into the vessel placed in front of the furnace to receive it, whilst the residues are drawn out through the working doors. The ore is usually introduced into the furnace through the arch at the top by means of a hopper.

The construction of an English furnace, as employed at Stiperstones in Shropshire, is shown in the accompanying figures (Figs. 187 to 190). It is trapezoidal in shape, having three working doors *i*, *i*, *i* along each of the longer sides. The hearth H is 11 feet long and 9 feet broad in the middle, and is composed of residual gray slags. It has a thickness of 4 inches at the back, 12 inches at the fire bridge, 14 inches at the flue, 2 feet 6 inches at the front of the sump, and 8 inches at the back of the same. An arched roof provided with an opening, with a hopper *l* for introducing the charge, covers the fireplace and hearth. The fireplace is on the longer of the two short sides of the furnace, the grate *z* lying nearer to the back than the front of the furnace, so that the flame does not pass across the well. The stoke-hole *g* is at the back of the furnace, and a small chimney *d* is placed here to convey away the steam from the ashpit, the bottom of which is covered with water. The grate is 2 feet 6 inches broad and 4 feet 6 inches long. The fire bridge P is air-cooled, and is 4 feet long and 2 feet broad. Opposite the fireplace are two flues, *c*, *c*, which communicate with

the chimney by means of the passage *e*. The flue at the back is slightly larger than the front one, so that the flame passes chiefly over the upper part of the hearth, avoiding the well; both flues

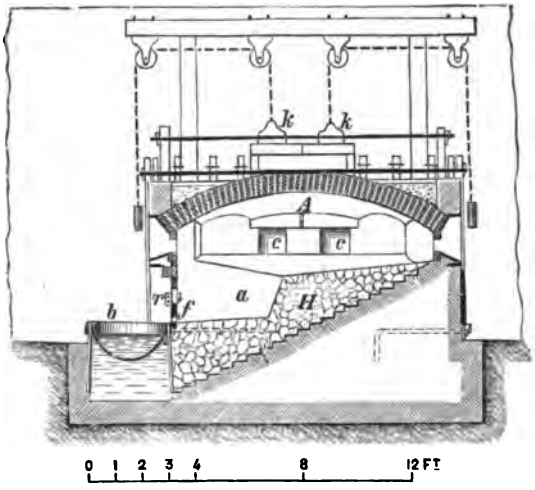


FIG. 187.

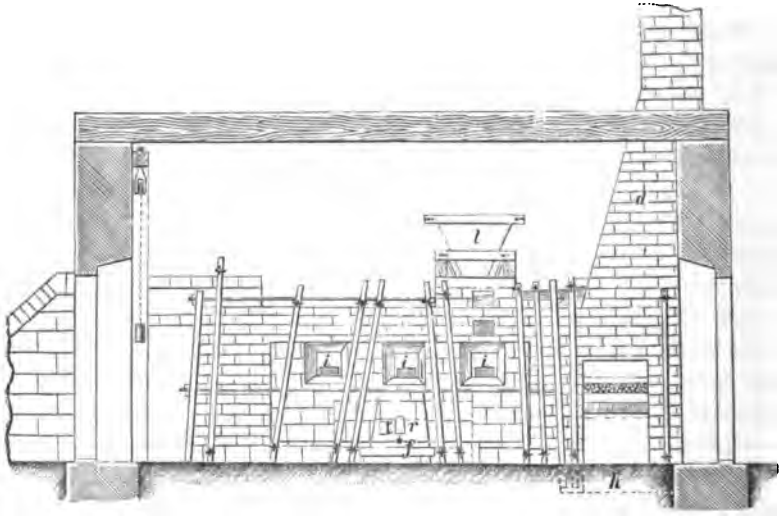


FIG. 188.

are provided with dampers for regulating the draught. The tap-hole *f* is situated 8 inches above the bottom of the hearth; over it is an opening, which can be closed by a door, for the purpose of admitting air into the furnace.

The charge for such a furnace weighs about 1 ton, the smallest charge worked in an English furnace being one of 16 cwt. The ore is spread in a layer of from 4 to 6 inches in thickness on the hearth.

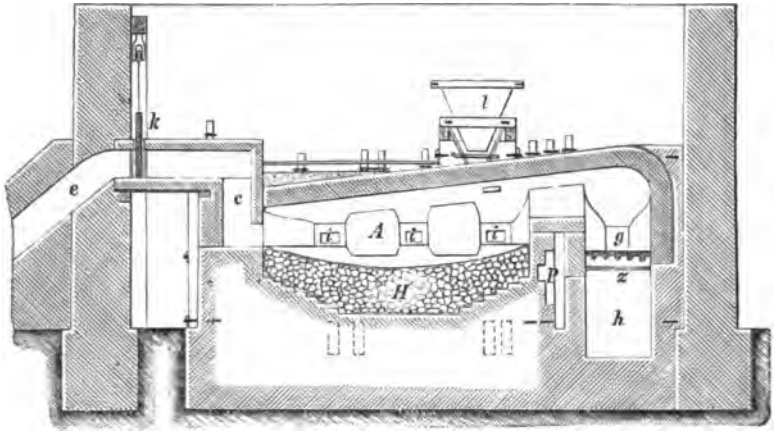


FIG. 189.

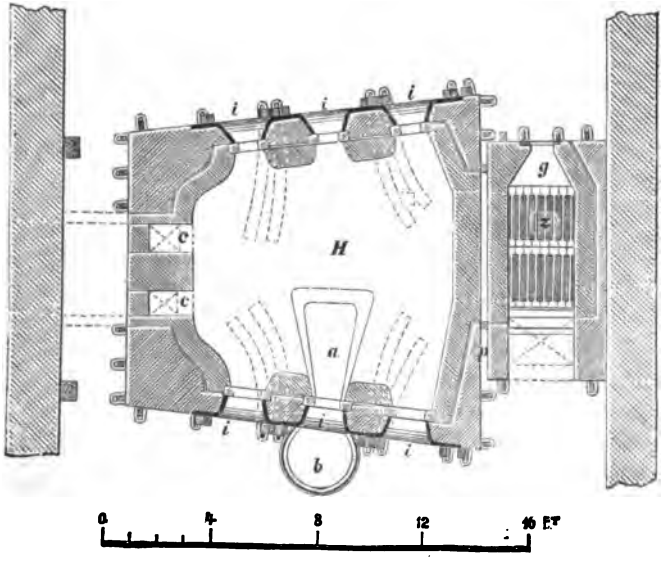


FIG. 190.

The actual conduct of the process varies in different works and depends chiefly upon the foreign substances present in the ores, the weight of the charge, and the amount of lead which it is considered

desirable to allow to remain in the residue. In many works a single reaction stage follows a shorter roasting period, whilst at other places the residue is submitted to a series of roastings followed by periods of reaction at short intervals. The roasting is conducted with the working doors open or only partly closed, the reaction stage with the doors shut and the temperature raised. The cooling and stiffening of the mass rendered fluid during the reduction period is effected by mixing slaked lime with it. The more carefully the initial roasting is conducted, the greater is the direct yield of lead.

The duration of the process is from 5 to 9 hours, depending upon the nature of the ore, the weight of the charge, and the degree of removal of the lead from the residue. The time occupied in the roasting or in the reaction period is very variable, and only in few instances is the working of the charge effected by a single roasting and reaction. Usually the charge is roasted for from 2 to 3 hours, then the reaction period follows at a higher temperature. Then the mass is stiffened or *set up* by the addition of lime, again roasted at a lower temperature for a short time, the roasting being followed by another reaction period, and the operations are repeated in this order until no more lead can be obtained from the residue. The fuel used varies from 50 to 80 per cent. of the weight of the charge.

The English process is in use in Flintshire, Shropshire, Derbyshire, Cornwall, and at Linares and Cordova in Spain.

At Stiperstones the process is conducted as follows.[1] The ore in charges of little over a ton is placed into the furnace, still red-hot from the preceding operations. This is roasted at an increasing temperature with constant and thorough stirring for about 2 hours, only the two doors nearest to the flue being kept open during this period. The other two doors are now opened, as well as the ashpit and fireplace doors, the damper is raised, and the highly heated charge is allowed to cool for half an hour. The sintered mass lying close to the fire bridge is broken up and well mixed, the working doors are closed, the damper partially lowered, and the first reaction stage is brought about by urging the fire. This lasts from 55 to 60 minutes. Then the mass is again cooled, and undergoes a fresh roasting with the working doors open, and the firing slackened; the cooled mass is stirred up, the cooling and stirring taking about half an hour. During this time the lead collected in the well is tapped off into the cast-iron pot in front of the furnace, the tap-hole being then stopped from the inside by a clay plug. After

[1] *B.-u H. Ztg*, 1863, pp. 243, 251, 261, 265.

2 hours' heavy firing with closed doors the second reaction stage is ended. Then follows a cooling period of 20 minutes. The portions of the mass, which in spite of all care have been liquefied and have flowed into the well, are set up with lime and pushed back on to the hearth. The residue is collected together as near as possible to the firebridge and some small coal is mixed with it. It is now strongly heated with closed doors for about a quarter of an hour in order to extract the remaining lead, and it is then drawn out of the furnace. The duration of the entire process is 7 hours, the coal used being 11 cwt. to 1 ton of ore. Two workmen are required, and the loss of lead is stated to be 12 per cent.

At Holywell, in Flintshire, a similarly arranged furnace is used, and the charge is the same. According to Percy[1] the charge is first roasted for an hour and a half, all doors being open. Then the fire is urged with two only of the doors open for 2 hours, the mass being occasionally stirred, when the reaction between the oxide, sulphate and sulphide takes place. At the end of this time firing is carried on vigorously for 40 minutes, so as to melt most of the charge down into the sump or well of the furnace. Then the doors are opened and the charge cooled and raked over, the molten mass in the well is set up with lime, and pushed back on to the hearth near to the fireplace, together with the mass remaining on the hearth. A further reaction stage, lasting about 50 minutes, now ensues, the temperature being raised during the last 20 minutes so that the mass fuses, and after the expiration of this period the fluid residue is stiffened with lime and raked out of the furnace. The lead produced is tapped from the well into the pot as at Stiperstones, and at both places it is purified by poling. The working of a charge occupies 6 hours. According to Percy[2] the amounts of lead oxide, sulphate and sulphide present in the charge at different stages of the process as well as the quantity present in the residue are as follows:—

State of combination of the Lead.	Percentages of Lead present, counting from the time of the introduction of the charge.				Percentage of Lead in the residue.
	after 1½ hrs	after 3½ hrs.	after 4½ hrs.	after 4¾ hrs.	
PbS	63·82	53·32	24·76	4·35	0·90
PbO	27·25	31·49	43·12	47·50	48·87
$PbSO_4$	3·82	4·78	6·94	14·02	9·85
Total metallic lead	83·16	78·66	66·22	47·86	52·88

[1] *Lead*, p. 232.

[2] *Lead*, p. 235.

At Alport, in Devonshire,[1] the English process was carried on as at Stiperstones and Holywell, but with smaller charges (16 cwt.) and in a smaller furnace. The ores contain 76 to 80 per cent. of lead, partly present as carbonate, which shortens the roasting period. The process is conducted as in Flintshire, only, owing to the ores containing heavy spar, an addition of fluor spar is made, whereby a freely-fluid slag is produced, which is run out of the furnace by a special slag tap-hole placed over the one for the lead. As in Flintshire an addition of lime is made for the purpose of stiffening the charge. The residue is drawn out of the furnace by the working door, and the fluid slag is tapped off. The process lasts from 4½ to 5 hours, and it is attended with a loss of 10 per cent. of lead. Only the richer slags, with at least 6 per cent. of lead, are worked up in the slag-hearth.

At Snailbeach, near Shrewsbury, according to the same authority, the process was conducted more slowly in order to obtain a higher yield of lead. The reverberatory furnace is provided with 5 working doors, 2 at the front, and 3 at the back. The well is situated at the flue end of the front side of the furnace, and consequently the charge can be spread and heated evenly, and the lead in the well is better protected from the action of the hot gases. The charge amounts to 1 ton, and it is first submitted to 2 hours' roasting with frequent stirring, followed by a period of reaction lasting 15 minutes This is then followed by a 4 hours' roasting and a reaction period of 15 minutes. The temperature is then increased, and with frequent stirring the mass enters on a reaction stage of 2 hours' duration. The remainder is then stiffened with lime, thrown up in front of the fire bridge and the lead in it liquated out. The residue, amounting to one eighth of the charge, and containing 40 per cent. of lead, is afterwards smelted in a low slag-hearth.

The working of a charge occupies 9 hours, 10 parts of coal being used to 16·8 parts of ore, each furnace requiring 2 men. The loss of lead is stated to be about 6 per cent.

The English process is not to be recommended, on account of the quick but incomplete roasting, and the large loss of lead on account of the high temperature employed. With certain modifications, it can, however, be made very suitable for rich ores free from silica, these modifications being that still larger furnaces should be employed (*see* the Tarnowitz furnace, page 304), the roasting conducted at a low temperature as slowly as possible, until for one molecule of sulphide there are formed one molecule of sulphate and two

[1] Percy's *Lead*, p. 240.

molecules of oxide; the reaction period should not be carried on so as to melt the charge, and the residue should only be deprived of its lead as far as this can be effected without much loss of metal, the rest of the lead being obtained from it by smelting with a reducing agent in the slag-hearth.

THE TARNOWITZ PROCESS

This process is the Carinthian process worked in an English furnace with very large charges, the last or slag-reduction (*bleipressen*) stage being either omitted or considerably curtailed. By conducting the process according to the Carinthian method, and interrupting it at the end of the *rabbling* stage, a pure lead is obtained with only a small loss, whilst the loss of lead which takes place during the subsequent process for the extraction of the lead from the residue is done away with, and the various foreign metals (antimony and copper), which would be reduced by carbon in this latter stage and pass into the lead, remain behind in the residue.

By employing a large furnace, the advantages of the English process are secured, viz., a large output and a small expenditure for fuel and wages. It is, however, impossible to avoid leaving a large percentage of lead (33 to 50 per cent.) in the residues, which are, therefore, smelted in shaft furnaces, in which the loss of lead is considerably smaller than in the slag reduction, as carried out in the reverberatory furnace. If the ore is argentiferous, the silver is concentrated in the portion of the lead first produced.

The process is employed at Friedrichshütte, Tarnowitz, and at the Walther-Kroneck Works at Schoppinitz, in Upper Silesia. At Mons, in Belgium, a similar process, developed independently of the Friedrichshütte method, is employed.

The process, as worked at Friedrichshütte, is peculiar, inasmuch as a fourth of the ore employed contains a considerable proportion of zinc blende, and has consequently to be submitted to a preliminary roasting in a long-bedded calciner (*fortschaufelungsofen*), plumbiferous slags or residues being added to assist the process.

LEAD SMELTING AT FRIEDRICHSHÜTTE

The ores smelted at present contain on an average 70 per cent. of lead, 0·003 per cent. of silver, 4 to 5 per cent. of zinc (present as blende), in addition to small amounts of pyrites, spathic iron ore, calcite, magnesite and zinc carbonate. They are free from copper, arsenic and antimony.

The construction of the furnace is shown in the Figs. 191 to 194. It differs from the Stiperstones furnace in having four working doors on

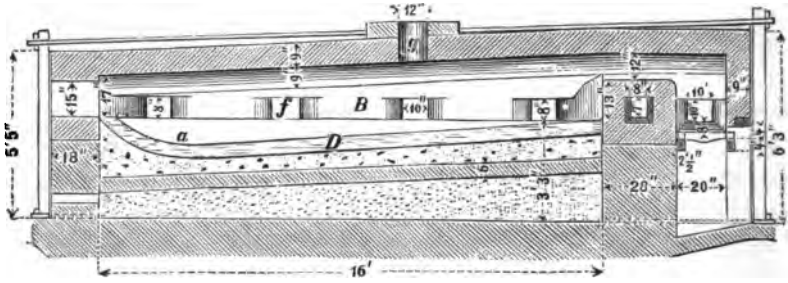


FIG. 191.

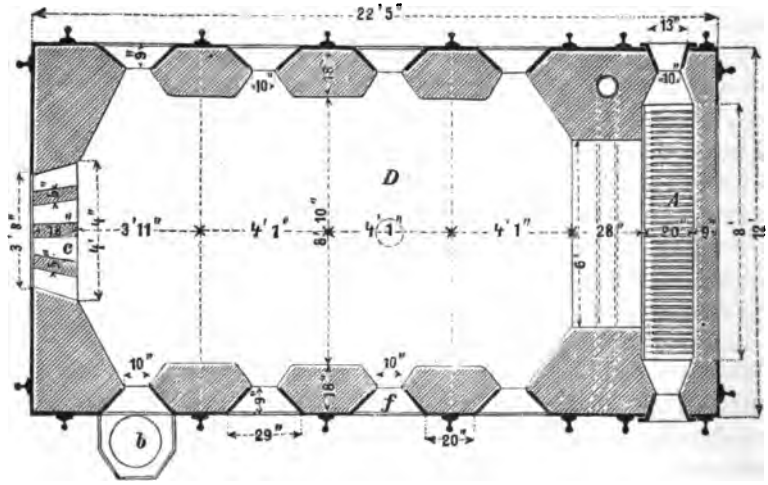
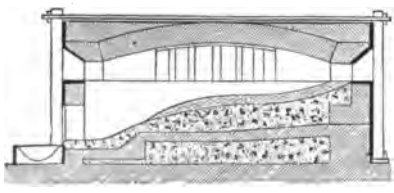
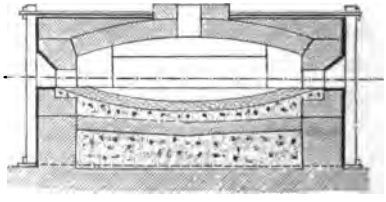


FIG. 192.





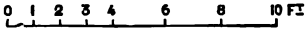


FIG. 193. FIG. 194.

each of its longer sides, whilst the hearth has a gradual slope towards the well, instead of a sudden fall, and the well itself is not placed in the

centre of the front of the furnace, but at the end nearest the flue. The hearth is 16 feet 6 inches long and 9 feet broad. It was formerly composed of iron refinery slag melted over a brasque bottom, whilst it is now made by heating together reverberatory furnace residues and lime until the mass becomes pasty. The brasque bottom rests on a layer of bricks, resting in turn on a bed of sand. The hearth proper is 3 to 4 inches thick, as also is the bed of brasque composed of 3 parts coke and one part clay.

The fireplace, situated at one of the shorter ends of the furnace, can be fired from either of the longer sides of the same. The grate is 20 inches broad and 8 feet long. The fire-bridge, which is hollow for air-cooling, is 6 feet 3 inches long and 29 inches broad. The flue lying opposite the fireplace, 4 feet 6 inches broad and 15½ inches high, is divided into 4 slits by brick partitions. The furnace gases passing through it are conducted through an extensive system of flue dust chambers and thence into the stack. The lead which collects in the well is tapped out into a pot placed in front of the furnace. The charge is introduced into the furnace through a hole in the arched roof, and the residue is pushed through an opening in the hearth bottom, covered during working with an iron plate, into a vessel placed beneath the furnace to receive it.

The charge worked at present weighs 2½ tons.

The ore first undergoes a 4 hours' roasting, being spread in a layer 3 to 4 inches thick, the temperature being kept at a dull red heat (500–600° C.), and the mass being rabbled from 8 to 10 times. The fire is then urged and the reaction stage follows, the mass being thoroughly mixed by stirring. At this stage, in order to assist the reaction, 10 to 12 cwts. of various kinds of residues from the smelting works, but all containing lead oxide, are added. These consist of flue dust, lead oxide containing zinc from the purification of the lead remaining after its silver has been removed by Parkes's process, skimmings containing lead, litharge, and formerly cerussite.

The reaction period lasts altogether 7 hours. During this time the fusion of the mass is prevented by regulating the air supply and by additions of lime. By thoroughly stirring the mass with the doors open, it is cooled from time to time, and though the production of lead is thereby interrupted, oxidation of the undecomposed lead sulphide is simultaneously promoted. By urging the fire and closing the doors, the mass is again brought to the temperature at which the formation of lead begins afresh.

The cooling of the charge and the subsequent reheating are repeated several times, at intervals of 1½ to 2 hours. Three hours

from the commencement of the reaction stage so much lead has collected in the well that the first tapping takes place. The lead produced (virgin lead) is proportionately rich in silver (0·17 to 0·2 per cent.). Other tappings follow at intervals of from 1½ to 2 hours, yielding each time less lead, which is also poorer in silver. When no more lead is formed, which is the case after the reaction period has lasted for 7 hours, the residue is removed by being pushed through a vertical flue in the hearth into a crucible placed in a recess underneath. In this way the exposure of the workmen to lead fumes, which takes place when the residue is drawn out through the working doors, is prevented.

The residue, which constitutes 25 to 30 per cent. of the weight of the charge, contains 40 to 56 per cent. of lead, 60 to 65 per cent. of the total lead in the ore being obtained as metal, the remainder being in the residue, which also contains about 0·02 per cent. of silver. It is worked up in a slag-hearth for the recovery of its lead.

The process occupies from 11 to 12 hours, and requires 90 lbs. to 1 cwt. of coal for every 2 cwts. of ore smelted. Two men are required to attend to the furnace in each 12-hour shift. The lead loss is 4·45 per cent., but, counting the lead obtained from the residues and the flue dust, only 1·5 per cent.

At the Walther-Kroneck Works, at Schoppinitz, in Upper Silesia, the furnace is constructed with a fireplace on each of its shorter sides, the waste gases being drawn off in the middle of the furnace arch. The charge consists of 4 tons of ore containing 75 per cent. of lead. The roasting stage occupies 4 hours, the reaction period 6 hours. About 60 per cent. of the amount of lead present is obtained in the reverberatory furnace, and the residue is smelted in a Pilz furnace to recover the remainder of the lead.

The fuel used amounts to 55 to 60 per cent. of the weight of the charge.

THE BLEIBERG PROCESS AT MONS, IN BELGIUM[1]

This, like the Friedrichshütte process, is a combination of the Carinthian and English processes. The ore worked is galena, from Bleiberg, near Mons, containing 80 per cent. of lead, 0·76 per cent. of antimony, 0·006 per cent. of copper, 0·0145 per cent. of silver, and small admixtures of zinc blende, pyrites and quartz.

The furnace differs from the Friedrichshütte furnace, in that it possesses two fireplaces, one on each short side, and the waste gaseous products are drawn off through two flues in the centre of the furnace

[1] Habet, *Industrie belge*, Liége, 1878. *Revue univers*, 1877, No. 1.

roof, the arrangement being shown in Figs. 195 to 197. The hearth is 15½ feet long and 9 feet 6 inches broad, the two grates being each 6 feet 6 inches long and 16 inches broad. The fire-bridges are 2 feet broad and 1 foot below the roof. On each of the longer sides of the furnace are 3 working doors, *a*, *a*, *a*. The hearth slopes uniformly from each fire-bridge towards the centre, so that a channel is formed which slopes down towards the pot *s*, placed at the front of the

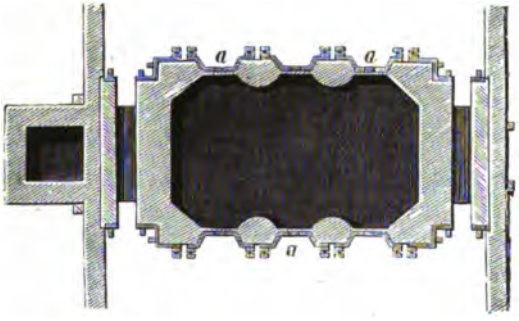


FIG. 195.

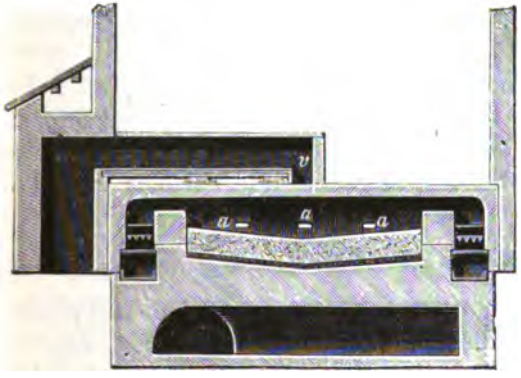


FIG. 196.



FIG. 197.

furnace before the middle working door. The waste gases pass through the openings *n*, *n*, into the flue *v*, and away to the chimney.

Two-ton charges are worked, the whole operation lasting 16 hours, 6 of which are occupied by the roasting, and 8 by the reaction stage. The process is so conducted that two thirds of the lead content of the ore are obtained in this furnace, the remainder being allowed to go into the residue. After the reaction stage is finished, the residue is fritted together by urging the fires and is then drawn out. It contains 66·36 per cent. of lead and 0·0024 per cent.

of silver, and is worked up together with flue dust and waste from the refining furnace in the slag hearth.

One ton of ore with 79·34 per cent. of lead yields 10½ cwts. of work lead, containing 0·0258 per cent. of silver, and 6½ cwts. of residue with 66·36 per cent. of lead and 0·0024 per cent. of silver. The coal used amounts to 40 per cent. of the weight of the ore, and the total loss of lead to 5·09 per cent.

The Tarnowitz process is the most suitable of all the air-reduction processes for rich ores free from silica, and is to be preferred for working these, if raw fuel is to be had cheaply.

THE FRENCH OR BRITTANY PROCESS

This process is a modification of the Carinthian processes, from which it differs in that larger charges (over 1 ton) are employed, the period of roasting is much longer, the residues are richer in lead, and the loss of metal is greater. It is suitable for ores containing up to 6 per cent. of silica, but is no longer employed on account of the attendant large loss of lead. It was formerly in use at Poullaouen in Brittany, Corfalie in Belgium, Albertville in Savoy, St. Louis and Escallotte near Marseilles, and at the Binsfeldhammerhütte at Stolberg.

In consequence of the prolonged roasting (7 hours) at a low temperature, necessitated by the presence of silica, more lead sulphate is obtained in proportion to unaltered sulphide than in the Carinthian process, consequently in the reaction stage lead oxide is formed in addition to the metal, according to the equation :—

$$PbS + 3PbSO_4 = 4PbO + 4SO_2$$

This lead oxide in its turn acts upon the unaltered sulphide still present forming lead and sulphur dioxide. As, however, oxide and sulphate are finally left, being present in excess, carbon in the form of coal or wood billets is mixed in with the mass in order to reduce the lead oxide to metal, and a part of the sulphate to sulphide, according to the equations :—

$$4PbO + 2C = 4Pb + 2CO_2$$
$$2PbSO_4 + 2C = PbS + PbSO_4 + 2CO_2$$

The sulphide and sulphate then react upon each other, so that either metallic lead is obtained or a mixture of lead and lead oxide, depending upon the proportions in which the two bodies were present. The lead oxide either reacts with more sulphide or is reduced by carbon.

In many cases the temperature during the reaction stage is raised so as to melt the charge, which is subsequently stiffened by the addition of lime.

As larger charges are worked by this method than in the Carinthian process, and as the formation of lead silicate cannot be altogether avoided, the residues obtained are richer in lead. The high temperature necessarily employed in the working of these large amounts of rich residue also makes the loss of lead greater than in the Carinthian process. The furnaces in which the process was conducted had either one or two hearths. In the latter case the roasting was carried out on the upper hearth, and the reaction, as well as the extraction of the lead from the residue, on the lower one. The final residues were worked up either in slag-hearths or reduced by iron in reverberatory furnaces.

As an example of the process, the method of working formerly employed at Poullaouen, in Brittany,[1] may be briefly considered.

The ore was galena with 5 per cent. of quartz, and a small admixture of zinc blende and pyrites. The furnace had one hearth having three working doors in the front longer side only, the tapping pot being placed under the centre one. The hearth composed of clay saturated with molten ore was 11 feet long and 6 feet 6 inches broad. The fireplace was on one of the shorter sides of the furnace and the flue opposite to it, the grate being 4 feet 3 inches long 20 inches broad, and the fire-bridge 22 inches broad.

The charge weighed 26 cwts., and was first roasted at a low temperature for 5 or 6 hours. Crusts of lead sulphate formed on the surface of the ore, and were broken up and mixed in with the rest of the charge. When the roasted mass began to cake together, and the first drops of lead appeared, in consequence of the action of the sulphate on the galena, the fire was urged so as to render the mass pasty, but not sufficient to make it fluid, and the reaction stage set in.

For the purpose of reducing the lead oxide and the excess of lead sulphate produced, pieces of wood or of lean coal were added, and the mass stirred at short intervals. The first tapping took place 4 to 5 hours after the commencement of the reaction stage, and was followed after an interval of 1½ to 2 hours by a second tapping, the residue being then drawn out of the furnace. The latter amounted to 33 per cent. of the charge, and contained 38 to 39 per cent. of lead. The reaction stage lasted 8 hours, and the whole operation 16 hours; 176 cubic feet of wood and 6 cwts. of coal were used, and the labour of

[1] *B. u. H. Ztg.*, 1863, pp. 367, 368. *Ann. des Mines*, 6th series, 13, p. 335.

two men was required. The residues were smelted with iron in a reverberatory furnace, together with silver ores and plumbiferous furnace products.

Of the lead in the ore 71 per cent. was obtained in the reverberatory furnace; 19 per cent. of the lead in the residues was recovered, and the entire loss of lead amounted to 10 per cent. of the total lead present in the ore.

The French process is no longer used, partly on account of the exhaustion of the ore deposits, and partly because it has been superseded by the roasting and carbon-reduction process, which is superior to it in every respect.

According to the foregoing statements it will be seen that the air-reduction process is chiefly employed where fuel can be cheaply obtained and the ores are rich and free from quartz, the Tarnowitz, or a method conducted on similar lines, being the best way of carrying it out.

SMELTING BY THE AIR-REDUCTION PROCESS IN HEARTHS

The air-reduction process, when worked in hearths, is attended with a larger loss of lead than when it is conducted in reverberatory furnaces, and is more injurious to the health of the workmen on account of their exposure to the lead fumes.

The hearths are worked with a blast of air, and either natural fuels, such as wood, peat or coal, can be employed, or a carbonised fuel like charcoal.

The hearth processes are distinguished from others by the fact that the charge and the fuel do not rest on a solid bed but float on a bath of molten lead, with which the hearth is almost filled, otherwise the iron of which the sides of the hearth are composed would be attacked. A further difference between these and reverberatory furnace processes is that the lead is obtained from the ore by the reducing action of the carbon of the fuel, in addition to that produced by the interaction of sulphide with sulphate and oxide.

The two stages of roasting and subsequent reaction are not distinct, but the various reactions are all taking place at the same time; part of the ore is being roasted, the reaction between sulphate and oxide and unaltered galena is going on, as well as the reduction of lead oxide by carbon.

The ore must be of the size of peas or better still in pieces as large as a hazel nut. Smaller pieces are to be avoided, otherwise the ore readily falls to powder. Ores in fine powder must first be

sintered together before treatment in the hearth. From 11 to 33 lbs. is the quantity treated at one time.

The process is so conducted that the charge on the hearth never melts. In order to prevent this occurring, the blast is stopped, portions of the charge are withdrawn at short intervals from the furnace, the poor slag separated from them, and after subsequent cooling, usually with an addition of lime to stiffen them, they are returned to the hearth.

In order to protect the workmen from the considerable amount of lead fume which is produced, an arrangement is fixed over the hearth in order to carry it away, the fume being deposited afterwards in capacious condensers.

The hearth is a rectangular cavity, the bottom and sides of which are made of cast iron. In many cases the front side is composed of a mixture of bone ash and crushed galena, this being impervious to metallic lead. In front is a sloping plate, the so-called *workstone*, and in it is a narrow channel along which the lead, flowing over from the hearth, finds its way into a heated cast iron pot. Over the hearth are placed hoods in connection with flues, in order to carry off the lead fume. In many hearths there are extensions of the back and side walls made of cast iron, which are either air- or water-cooled. When air-cooling is employed, the blast is led through the parts to be cooled, though by employing the blast thus heated the loss of lead by volatilisation is considerably increased. On this account air-cooling has in most cases been replaced by water-cooling, except in those cases where a part of the lead is purposely volatilised and the fume, after cooling, collected in bags and afterwards worked up for paint (Bartlett's process).

Hearths can be divided into four classes:

1. The Scotch hearth.
2. The air-cooled American hearth (Rossie furnace).
3. The water-cooled American hearth.
4. The Jumbo hearth or Moffet hearth with both air- and water-cooling.

The Scotch hearth is shown in the accompanying Figs. 198 to 202. The first two figures represent a hearth, the front wall of which is made up of a mixture of bone ash and crushed galena. A is the hearth proper, 22 inches long, 19 inches broad, and 12 inches deep. The bottom ($2\frac{1}{2}$ inches thick), both sides, and the back are of cast iron, the front wall of the mixture just mentioned. Against this front side or so-called *dam* fits a sloping cast iron plate (*workstone*) with turned up edges and a channel *b*, and in front of

this is placed the cast iron pot C which is kept hot. The lead reduced from the ore overflows the dam when the hearth is full and finds its way along the channel *b* into the pot C. The blast is introduced at the back, the nozzle of the tuyere resting on the square cast iron prism or *backstone d*, upon which lies the cast iron piece *e*, the so-called *pipestone*, which is provided with a hole for the tuyere. On the sides of the hearth are similar cast iron pieces. Twelve inches above the dam is placed the *forestone* of cast iron. Over the hearth is an open hood connected with the fume chambers.

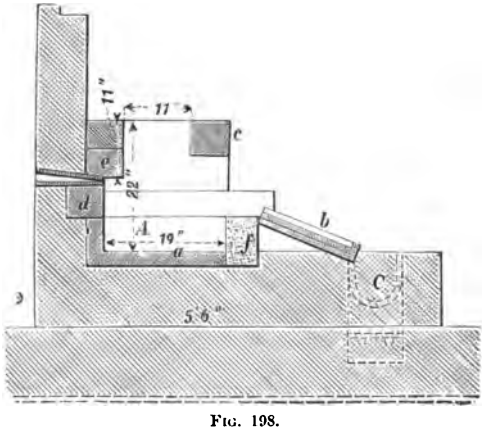


FIG. 198.

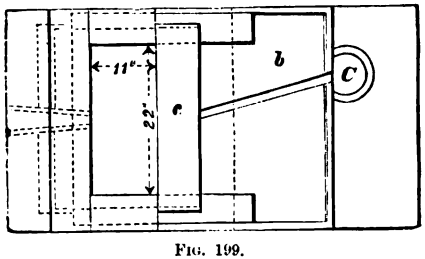


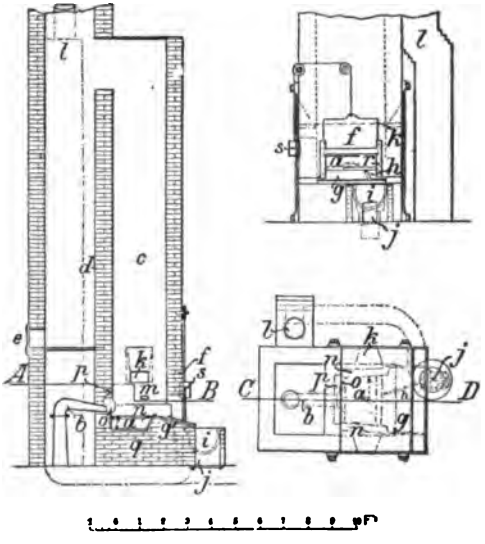
FIG. 199.

Figs. 200 to 202 represent a furnace constructed entirely of cast iron, with fume collector and a sliding door in front of the hearth, formerly in use at the works of Messrs. Cookson & Co. near Newcastle-on-Tyne.[1]

The hearth *a* is constructed entirely of cast iron, and with the cast iron workstone *g*, rests on brickwork. The channel *h* in the

[1] *Eighth Annual Report of the Local Government Board*, 1878–79. Supplement containing the Report of the Medical Officer for 1878. London, 1879, p 281.

work stone conveys the lead flowing over from the hearth into the cast iron pot *i*. The hearth holds 2 tons of lead. On each side are cast iron pieces *n*, and on the back the cast iron block *o* rests, having a space in it for the tuyere *b*, the nozzle of which lies 2 inches above the level of the lead surface on the hearth. On the block *o* a wider cast iron piece *p* rests, and *m* is a cast iron bar placed over the front of the hearth; *c* is the chimney for the fume, and *d* is a dust-collecting chamber, the flue dust being removed by means of the door *e*. The fuel can be dropped on to the hearth through the



FIGS. 200, 201, and 202.

door *k*, while the ore is added from the front of the hearth, which can be closed or opened by the sliding door *f*.

The disadvantage of this hearth is that uninterrupted work in it is not possible, as the sides become heated, and it is necessary to allow time for cooling after the working up of each charge. It is employed in England and Scotland, peat or bituminous coal being used as fuel.

The American air-cooled hearth or Rossie furnace was formerly employed in New York State, but was abandoned on account of the large loss of lead by volatilisation; it is still employed at Bleiberg, in Carinthia.

The construction of this furnace is shown in Figs. 203 and 204. The hearth is composed of cast iron plates, the cavity being 2 feet

long, 2 feet broad, and 1 foot deep. In the front it is furnished with a workstone C, in which is a channel *d*, to convey the lead from the hearth into the heated iron pot D. At the back and both sides of the hearth is the double walled air space B, formed partly by an extension of the sides. Into this space the blast enters at *a* and leaves it at *b*, passing along the tube in the direction of the arrows to the tuyere *c*. At Rossie, wood was used as fuel. In a similar furnace at Bleiberg 2 tons of lead ore were worked in 12 hours.

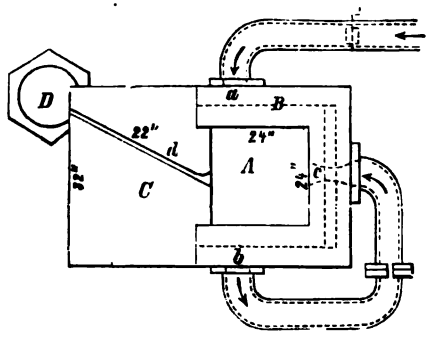


FIG. 208.

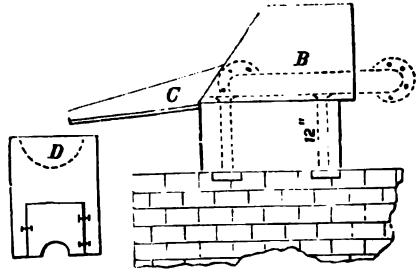


FIG. 204.

The water-cooled American hearth is shown in the Figs. 205 and 206. It has a cast iron hearth set in masonry. Above the back and both sides is a hollow cast iron chamber through which water circulates, the water entering by the tube *b* and flowing away through *c*. At the back of the water casing is the air chamber *d* communicating with the blowing apparatus and delivering the air through three nozzles on to the hearth. Wood, coal or charcoal is employed as fuel.

This furnace is employed in Missouri, U.S.A.[1]

[1] Williams, "Industrial Report," *Geol. Survey of Missouri*, 1877, p. 36. *Trans. A.I.M.E.* v. p. 324. Broadhead, *Geol. Survey of Missouri*, 1873–74, p. 492.

The Moffet hearth or Jumbo furnace is also employed in the United States and in England, and consists of a double hearth partly air- and partly water-cooled. Figs. 207 to 209 show its construction.[1]

The furnace is supported on cast iron pillars, so that the cavity of the hearth is cooled underneath by the air. The hearth is divided

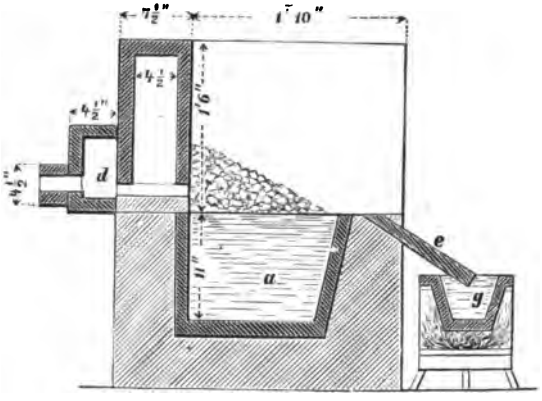


Fig. 205.

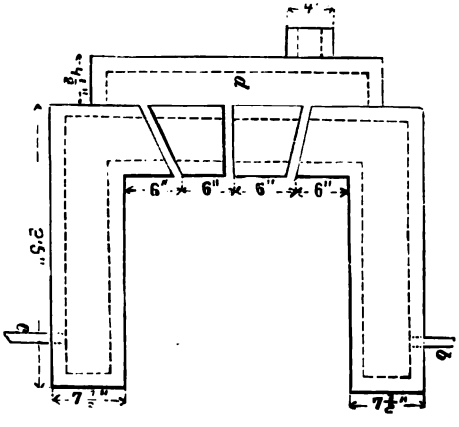
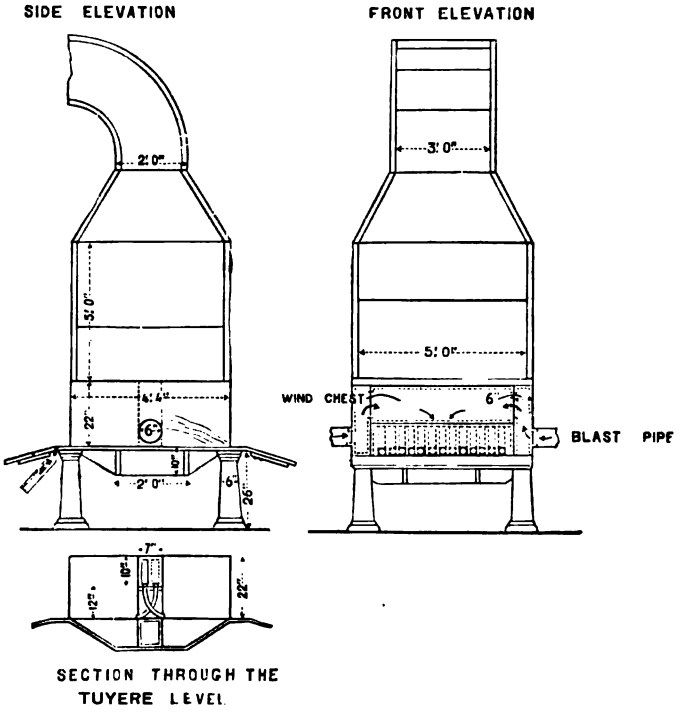


Fig. 206.

into two parts by means of a hollow cast iron partition lying on the bottom, so that each part forms a separate hearth which can be worked independently of the other This partition box serves as the back of

[1] Dewey, *Trans. A.I.M.E.* xviii. p. 674. Clerc, *Engin. and Min. Journal*, July 4, 1885. Ramsay, *Sc. American Supplement*, May 14, No. 593, 1887. *Trans. of the A.I.M.E.* Feb., 1890.

both hearths, and has a hole in its lower part by which it is filled with molten lead. Upon this a hollow cast iron box rests in which water circulates, and above this is the air chest, also of iron, divided lengthwise into two parts. From both of these parts the air passes through a series of seven copper nozzles through the water-box and delivers warm air on to the hearth. This hearth is used mainly for the extraction of lead, but also serves for the manufacture of white paint from the fume (at Joplin in Missouri).



Figs. 207, 208, and 209.

The manner of conducting the process in the various hearths is almost identical, as long as the object is not to obtain the fume for use as a pigment.

On to the hearth, which has previously been almost filled with lead, some coal is strewn and then the fuel (coal, peat, wood or charcoal) is piled upon it. When the fuel is well ignited and in a glowing state the residue from the previous operation, called *browse* in England and Scotland, is put on to it. As soon as lead begins to separate out, a quantity of ore, varying according to the size of the hearth from 11

to 33 lbs. mixed usually with a little lime (1½ to 2 per cent.), is thrown on to the glowing mass and covered with a small portion of fuel. After 10 or 15 minutes the underside of this mass is sintered together, and it is then broken up and withdrawn on to the workstone, the top portion of the charge now sinking down in the hearth. On the workstone the slag is separated from the incompletely decomposed ore (*browse*) and the latter, mixed with a fresh quantity of ore and a little slaked lime, is put back into the hearth, the separated slag being collected and afterwards worked up in the slag-hearth. After 5 or 10 minutes the mass is again broken up, the lower partially smelted portion being withdrawn from the hearth and treated as before.

The various operations of breaking up the charge, drawing out the residue, and separating the slag from it and then replacing it in the hearth are repeated at intervals of from 5 to 10 minutes.

In those Scotch hearths which are not provided with any cooling arrangement, after 8 to 12 hours working the hearth becomes so hot that an interval of some 5 hours is necessary in order to allow it to cool down, this interruption of work being unnecessary in hearths which are cooled. The separated lead trickles through the fuel into the hearth, and when this is quite full it overflows and passes along the channel in the workstone to the vessel placed in front to receive it.

A hearth with a large output requires the labour of three, a smaller one of two, men.

In a Scotch hearth at Wensleydale (Yorkshire)[1] 192 cwts. of ore were smelted in a week in shifts of from 6 to 8 hours, with a consumption of 6 cwts. 3 qrs. of coal and 24 bushels of peat. The yield of lead was 142 cwts. 3 qrs. 18 lbs., or 74·44 per cent., and 12 cwts. 2 qrs. 14 lbs. of grey slags were produced and 3 cwts. of *browse*, which, however, was the same as the amount of *browse* available at the beginning of the operation. In each 8 hours shift 32 cwts. of ore were treated.

In an American air-cooled hearth (Rossie furnace) at Rossie, New York, 4½ tons of ore were worked in 24 hours, producing 3½ tons of lead, with a consumption of 2 cords of wood, the direct yield of lead being 73·88 per cent. At Bleiberg in Carinthia 2 tons of ore were worked every 12 hours in a Rossie hearth, the loss of lead being about 2 per cent. greater than in the Carinthian process.

In an American water-cooled hearth at Granby, Missouri, 4½ tons of ore were smelted in 24 hours, using 27·6 bushels of charcoal, and

[1] Percy's Lead, p. 283.

the direct yield of lead was not greater than 75 per cent. The slags worked up in a slag-hearth contained 30 to 40 per cent. of lead, and three men were required for each shift.

At the Hopewell works in Missouri a similar furnace was used, 3 tons of ore being worked in 24 hours with a direct yield of 73·2 per cent. of lead, three men being employed for each shift.

In the double hearth, with air-and water-cooling, 13½ tons of ore are worked in 24 hours with a consumption of 1 ton of coal, both metallic lead and lead fume for use as a pigment being produced. This process is used at the Lone Elm Mining and Smelting Company's works at Joplin, Jasper County, Missouri. The ore is galena, containing blende with 70 to 73 per cent. of lead. It is first smelted at a high temperature with an addition of 2½ per cent. of lime, the products being lead, lead slags and fume. A portion of the sulphide is converted by the oxygen of the blast into sulphate and oxide which react with the remaining sulphide, producing lead and sulphur dioxide. Part of the lead remains in the hearth and a portion is volatilised and oxidised, and a portion of the sulphide behaves similarly.

The lead fume after being cooled is collected in woollen bags, and forms a greyish powder, which, on being heated to burn off any soot or particles of coal, yields white crusts which are smelted in small slag-hearths, together with the slag from the first smelting of the galena. The lead and zinc volatilised are oxidised by air from a series of tuyeres placed at the upper part of the furnace. Metallic lead, slag and lead fume are formed in this furnace, and the fume after cooling is caught in woollen bags and forms a commercially valuable white pigment.

Of the entire amount of lead in the ore, 68 per cent. is obtained as metal, whilst part of the remainder is converted into fume, and a part finds its way into the slag.

The slags obtained by the hearth processes are smelted in shaft furnaces, usually in small furnaces known as slag-hearths, which will be described in detail in the chapter dealing with the methods of obtaining lead from plumbiferous residues.

Of the various forms of hearth that are in use, the one most to be recommended is the water-cooled hearth, provided that the object aimed at is to obtain the lead as metal and not partly as flue dust for the preparation of white pigments. If, however, in addition to lead it is desired to prepare these white pigments, as in the Bartlett process, then the hearth with air- and water-cooling is preferable.

Comparing together the hearth and reverberatory furnace methods, the disadvantages possessed by the former are the greater loss of lead

by volatilisation, the greater danger to the workmen from the fume, and the necessity for employing a blast of air.

The total loss of lead has not been exactly determined, but has been found to be about 2 per cent. greater in the Bleiberg hearths than in the Carinthian furnace in use there.[1]

As regards the yield of lead the hearth stands on a level with the processes that are carried on in large reverberatory furnaces, and in consumption of fuel has the advantage over the latter, though requiring more labour and that of a trained character.

The air-reduction process should, therefore, as a rule be carried out in reverberatory furnaces, hearths only being employed when it is desirable to volatilise part of the lead with a view to making pigments, or when motive power for the blast can be cheaply obtained, or when smelting is only carried on periodically, as happens when the ore is only delivered at long intervals. For argentiferous ores the hearth process cannot be recommended on account of the considerable loss of silver by volatilisation.

The Roasting and Reduction Process (*Röstreductionsarbeit*)

This method can be employed for galena containing an admixture of various bodies. Ores rich in silica and in bases which could not be smelted by the air-reduction process can be used, as well as galenas containing antimonial and arsenical compounds which could not be dealt with by the iron-reduction method.

The process consists in first roasting the ores in a specially constructed furnace and then smelting the roasted ore with fluxes and reducing agents in a shaft furnace, usually a blast furnace.

In the roasting, the lead sulphide is as far as possible converted into oxide. At the same time the sulphides of other metals are oxidised, and antimony and arsenic are as far as possible volatilised. In the roasting of galena it is impossible to prevent the formation of considerable quantities of sulphate; Plattner[2] obtained, by most careful roasting of powdered galena, 66·3 per cent. of oxide and 33·7 per cent. of lead sulphate. This lead sulphate, which would be reduced again in the blast furnace to sulphide, is in most cases converted into silicate at the conclusion of the roasting.

In the smelting of the roasted ore in the shaft furnace, the lead present as oxide is reduced by carbon, that present as silicate by

[1] *Oesterr Zeitschr.* 1883. *Vereinsmittheilungen*, No. 9.
[2] *Metallurg. Röstprozesse.*

iron and carbon combined. The sulphide present in the roasted ore, or formed in the furnace by the reduction of lead sulphate, is reduced by metallic iron, forming lead and ferrous sulphide. The other constituents, with the exception of gold and silver, must either be volatilised or slagged off, the gold and silver going into the metallic lead.

Of the various foreign substances present in the ores, zinc blende when in large amounts acts the most injuriously.

In the operation of smelting, zinc sulphide will find its way partly into the slag and partly into the matte if any be formed, making both substances less fluid, and carrying silver with it if the ores contained silver sulphide. In consequence of the less fluid condition of the matte and slag, they separate much less perfectly, and frequently a mixture of the two is obtained. Owing to the presence of iron a portion of the zinc is reduced from the blende, sulphide of iron being formed, and the free zinc volatilising, burns and increases the production of furnace fume. According to Plattner,[1] oxide and silicate of iron should decompose blende, the zinc oxide produced going into the slag, but this reaction appears only to take place incompletely.

As oxide of zinc is more easily slagged off than the sulphide, the latter must, as far as possible, be converted into the former during the roasting.

Zinc oxide alone forms an infusible silicate with silica, though it is easily taken up by basic ferrous silicate slags and, provided that the percentage of zinc is not too great, the resulting slag still remains sufficiently fluid to separate easily from the lead and matte. With large percentages of zinc oxide, the slag becomes thick and mechanically encloses some of the lead and lead matte. To a certain extent the ferrous oxide in the slag may be replaced by lime or baryta. A not inconsiderable proportion of the zinc oxide does not pass into the slag, but is reduced in the hottest part of the furnace to metallic zinc. This is volatilised and oxidised in the upper portions of the furnace by water vapour and carbon dioxide, and the oxide is partly deposited in the cooler parts of the furnace forming the so-called furnace accretions (*ofenbruch*), the furnace becoming so choked up in a comparatively short time that it has to be blown out. The zinc which is not deposited as *ofenbruch* or *furnace calamine* escapes with the waste gases carrying lead and silver along with it.

In consequence of these various ways in which zinc would inter-

[1] *Berg-und Hüttenm. Ztg.* 1854, p. 81.

fere with the smelting operations it must be got rid of as far as possible before the ores are smelted. If it is not possible to effect this by proper dressing operations, it must be separated from the roasted ore. This can be done by converting the zinc into sulphate and lixiviating, either roasting the ore and then dissolving out the neutral sulphate with water and the basic sulphate and the oxide with sulphuric acid, or roasting it completely to oxide and dissolving this with sulphuric acid or other solvents, or else the zinc may be reduced and volatilised with a portion of the lead, as in the Bartlett process.

Compounds of arsenic, when present in large amounts, give rise to the formation of a speiss during the smelting, containing copper, silver and some lead, in addition to arsenic, these metals being extractible only with difficulty, and then incompletely from the speiss. Part of the arsenic is also volatilised in the smelting, carrying with it lead and silver, and it is therefore necessary to eliminate arsenic as completely as possible during the roasting stage. Small quantities of arsenic also find their way into the lead produced.

Antimony has less tendency to give rise to the formation of a speiss than it has to alloy with the lead which mixes with it in all proportions. In the smelting it is partially volatilised, carrying with it both lead and silver. Unless it is specially desired to produce an antimonial lead, it should be got rid of as far as possible in the roasting, as even in small quantities it acts injuriously upon the softness of the metal produced.

Copper, provided there is not any sulphur present during the smelting process for it to combine with, finds its way into the lead, from which it has to be separated by a special process of purification. If it is present in the ores in quantity sufficient to make it worth while, the process is modified, the ore being submitted to a less thorough roasting and a part of the sulphur being retained, so that in the smelting, a regulus is formed containing the copper, together with some silver sulphide, if the latter be present, as well as other metallic sulphides.

From this regulus the lead and copper are obtained by a special roasting and smelting process, the silver passing partly into the copper, partly into the lead.

The roasting and reduction process yields a less pure lead than the air-reduction method, because portions of the oxides of foreign metals are reduced, and the reduced metals alloy with the lead.

The Roasting of the Ores

The ores are roasted either in the state of lumps or of powder, lump roasting, which was formerly the chief method, being now only resorted to under special circumstances.

In roasting a pulverulent mixture of galena with copper pyrites, zinc blende, quartz, spathic iron ore and gangue, which usually forms the raw material for the roasting and reduction method, the sulphur of the sulphides forms sulphur dioxide as soon as the requisite temperature is attained, and the metals are oxidised. A portion of the sulphur dioxide is converted into sulphuric acid, forming sulphates with the metallic oxides. As the temperature increases the sulphates of iron, copper, a part of the zinc sulphate, and finally the silver sulphate are decomposed one after the other. Zinc sulphate gives up only part of its sulphuric acid, forming basic sulphate, which is only completely decomposed into zinc oxide, sulphur dioxide and oxygen at a white heat. Lead sulphate remains unchanged, as it only parts with its sulphuric acid at a temperature about the melting point of iron. Antimony and arsenic compounds lose a portion of their antimony and arsenic in the form of arsenious and antimonious acids, but a larger part remains in the form of arseniates and antimoniates which are not further decomposed. Spathic ironstone is converted into magnetic oxide, calcium carbonate partly into calcium sulphate, whilst heavy spar is not altered.

The lead sulphate which is produced in roasting is, except in certain special circumstances, converted into silicate at the conclusion of the roasting operation. This is effected by adding quartz, if it is not already present in the ore, when, by raising the temperature until the mass melts, the silica drives off the sulphur trioxide of the sulphate, leaving lead silicate behind. If calcite be present in the ore, or calcium or barium sulphates in the roasted material, calcium and barium silicates will be formed, whilst the presence of spathic ironstone or of magnetic iron oxide, formed in roasting, would give rise to the production of ferrous silicate. By this combined roasting and melting, known as *schlackenröstung*, a fused mixture of oxides and silicates is obtained.

If the ores contain much copper, sufficient sulphur is allowed to remain in the roasted material to combine with it when in the blast furnace. In this case the conversion of lead sulphate into silicate and the melting of the ore at the end of the roasting operation are omittod, the roasted mass being only just sintered together so as

to avoid the inconvenience of smelting pulverulent ore in the blast furnace. In the same way with ores with a high percentage of silver, loss of silver through volatilisation is avoided by not fusing the mass at the conclusion of the roasting, it being only sintered together, or in rarer cases allowed to remain in the pulverulent form. In the pulverulent form, portions of the ore are easily carried away mechanically by the furnace gases, and as just mentioned, pulverulent ore is more difficult to smelt in the blast furnace than lump ore. The two methods are called respectively *sinterröstung*, when the charge is fritted together, or *staubröstung*, when it is allowed to remain in the pulverulent state.

The *schlackenröstung* and the *sinterröstung* are carried out in reverberatory furnaces, whilst the *staubröstung* can be conducted either in reverberatory furnaces, shaft furnaces or in muffle furnaces. In roasting lead ores in the lump form, neither the lead sulphate nor the sulphide can be completely decomposed, so that the roasted mass will always contain some undecomposed sulphide and sulphate, in addition to the oxides of the metals present. This method of roasting is employed with ores comparatively poor in lead but rich in pyrites, as well as with ores rich in pyrites and zinc blende. The roasting is performed in heaps, in stalls and in shaft furnaces.

THE PREPARATORY ROASTING OF THE ORE

The roasting of the ores is carried out in heaps or stalls, and in shaft furnaces, reverberatory, muffle and rotating cylinder furnaces, though the operation is best effected in reverberatory furnaces.

The employment of reverberatory furnaces enables the galena to be roasted both quickly and completely, and the lead sulphate to be converted into silicate, which, as previously mentioned, is effected by melting the roasting charge. The tall chimney which can also be used in connection with it serves to render the escaping gases less harmful. It has the disadvantage that the waste gases, being mixed with the products of combustion and diluted with nitrogen from the air, cannot be employed for the production of sulphuric acid. This drawback is, however, only felt when the ores are rich in pyrites, as the gases given off in roasting galena alone, even when special arrangements may be adopted, are too poor in sulphur dioxide to be used for sulphuric acid making. Pyritic lead ores are accordingly treated in shaft furnaces, and the evolved sulphur dioxide thus made available for the manufacture of the acid.

The advantages and disadvantages of heap and stall roasting have already been considered in connection with the roasting of copper ores (pages 26 *et seq.*). These methods are only occasionally employed with lead ores, when, for instance, pyritic ores, or ores containing blende, poor in lead, are to be roasted, or for the purpose of completing the roasting of ores which have already been treated in lumps in shaft furnaces. Lead ores containing copper pyrites or fahl-ore, which only require to be partially roasted, used also to be treated by this method.

On account of the disadvantages attending it, such as the length of time required, the incomplete separation of the sulphur, and the annoyance caused in the neighbourhood by the waste gases, it has been superseded by the reverberatory furnace method, and is now only employed for roasting poor ores, where the furnace process would be too costly, or for the final roasting of ores, which have been previously treated in shaft furnaces.

Shaft furnaces are only employed for roasting when the galena is associated with so much iron pyrites, or with copper pyrites and zinc blende also, that the gases from the roasting can advantageously be employed in the production of sulphuric acid. The roasting of galena in these furnaces is, nevertheless, incomplete, and it is necessary to finish the roasting in the case of lump ores by an after roasting in heaps, or, when the ore is in a fine state of division, in reverberatory furnaces.

Pyritic lead ores which, on account of their being easily sintered, cannot be treated in shaft furnaces, are quite exceptionally roasted in muffle furnaces, the evolved gases being used for the production of sulphuric acid. The production of lead silicate by the reaction with silica cannot be carried out in such furnaces.

Roasting in Heaps

Only lump ores can be roasted in heaps. Finely divided ores can to a certain extent be used as a cover; if they must be roasted in large quantities by this method, it is necessary to previously agglomerate them by mixing lime or ferrous sulphate liquors with them.

The object of roasting is not usually attained by a single operation, the process having usually to be repeated several times.

Heap roasting is employed with advantage at the Herzog Julius-hütte, near Astfeld, and at the Frau Sophienhütte, near Langelsheim, in the Lower Harz. At these places poor lead ores, containing

pyrites, zinc blende and heavy spar, the roasting of which in reverberatory furnaces would be too costly, are roasted three times in heaps. The zinc sulphide is converted as far as possible into neutral zinc sulphate, which is extracted from the roasted mass with water, basic zinc sulphate being only soluble in acids. During the first roasting a portion also of the sulphur of the pyrites is eliminated.

The ores have the following composition :—

Galena	9 to 12%
Zinc blende	27·5 to 30%
Copper pyrites	1 to 1·69%
Iron pyrites	11 to 16%
Gangue	44 to 47%

The gangue consists principally of barium sulphate (heavy spar).

The average content of metal and sulphur in the ores in recent years may be taken as follows :—

Sulphur	16 to 18%
Silver	0·011 to 0·015%
Copper	0·45 to 0·55%
Lead	9·98 to 10·5%
Zinc	18 to 19·5%
Iron	5 to 7%

The ores are subjected to three roastings. The smalls produced in the various roastings are rich in zinc sulphate, and are therefore extracted with water to dissolve out the neutral salt before being smelted. The liquors are allowed to crystallise, and are also worked up for calcined zinc sulphate.

The foundation for the heap consists of a bed, 1 foot thick, of well-rammed clay, upon which a layer of small roasted ore is spread to a depth of 4 inches. The heaps contain from 300 to 500 tons of ore. The ore is piled on a quadrangular bed, composed of cord-wood and brushwood 36 to 40 feet long on each side, channels being left for the access of air.

The largest pieces of ore which constitute the greater portion of the heap are first placed in position, then follow pieces of the size of the fist, then pieces as large as eggs, and then ore of the size of peas or hazel nuts, and lastly, if present, finely granular ore. The entire heap is covered with the fine roasted ore or smalls obtained by sifting the product from the first roasting, and has the appearance of a truncated pyramid of square horizontal section having a length of side at the base of 36 to 40 feet, and at the top of 12 feet 6 inches.

The shape of the heap and the arrangement of the bed will be gathered from the Figs. 210 and 211, where r is the bed and D

the cover. The semicircular depressions *v* in the top of the cover, serve to collect the sulphur arising from the decomposition of iron pyrites.

When the heap is ready it is ignited on the windward side. In this way the air, which is only admitted at the foot through the channels left in the bed, is deprived of most of its oxygen in the lower portions of the heap, and the hot gases given off from the top consist chiefly of nitrogen and sulphur dioxide. These hot



FIG. 210.

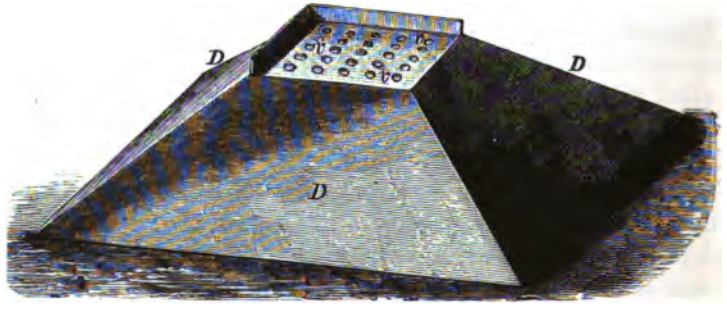


FIG. 211.

gases cause a decomposition of the pyrites in the upper portions, part of the sulphur of the same being driven off, and condensing in the liquid state on the upper surface of the heap. This is collected in the semicircular depressions *v*, which are formed by means of a leaden block and are lined with pyritic slimes or ore smalls; from these it is ladled out from time to time. The first portions of sulphur collect in fourteen days from the time of lighting the heap.

The first roasting lasts 6 to 7 months. Then follow second and third roastings in stalls provided with roofs. By employing this method of roasting, the dissolving away of zinc sulphate, or the

extinction of the heap which is now poor in sulphur, by rain, is avoided. The heaps have a square horizontal section, and contain over 500 tons of ore; on account of their low sulphur content, a covering of smalls is unnecessary.

After the first firing the lumps are separated from the smalls by sieving, and broken up in order to expose fresh surfaces in the next firing. The small ore is partly used as a cover for fresh heaps, and part of it is lixiviated. The same operations are gone through after the second or third roastings. The second roasting lasts 6 to 8 weeks, the third a month to six weeks. The smalls produced in the different roastings contain large quantities of neutral zinc sulphate. Those portions not employed as a covering in the first roastings are deprived of their zinc sulphate by extracting with water. The residue is dried in reverberatory furnaces and then smelted in shaft furnaces, together with the lump ore from the third roasting, which now contains only 4 to 5 per cent. of sulphur.

The following is an analysis of the roasted smalls :—

Silver	0·015%
Cupric oxide	1·34%
Lead oxide	14·44%
Zinc oxide	19·12%
Ferric oxide	22·95%
Sulphuric anhydride	15·95%
Sulphur	0·6%
Insoluble residue	17·08%
Alkaline earths, carbon dioxide, water, traces of manganese	8·505%

An analysis of the roasted lump ore gave :—

Silver	0·013%
Cupric oxide	0·93%
Lead oxide	10·02%
Zinc oxide	28·14%
Ferric oxide	13·64%
Sulphuric anhydride	16·62%
Sulphur	0·17%
Heavy spar	24·66%
Earthy matter	5·807%

The lixiviation of the roasted smalls is effected in cylindrical drums placed horizontally, and mechanically rotated, the sides being made of wrought iron and the bottoms of cast iron; they are 4 feet long, and 3 feet in diameter, and hold 1 to 1¼ ton of ore. The extraction is repeated 3 or 4 times, using for the first lixiviation the weak liquors from the previous operation and finishing with hot water. The first liquor at 50° B. is mixed with the second at 20° B., the

density of the mixture being 30° B., and this is then heated in pans of sheet lead resting on a cast iron plate to 80° or 90° C. for 24 hours and allowed to stand for 4 to 6 days. By this means (the process is known as *schieren*) the iron is separated out as a basic salt, and gypsum and other difficultly soluble bodies are precipitated. The liquor is now concentrated up to 50° B. in boiling pans and then cooled in pans, in which the zinc sulphate crystallises in the course of 5 or 6 days. For the complete roasting of 100 tons of ore 490 cubic feet of cord wood and 212 faggots of brushwood are used.

Roasting in stalls, like heap roasting, is only occasionally resorted to; like the latter it can be employed for the final roasting of lump ore which has undergone a preliminary roasting in shaft furnaces.

The Wellner stall without roasting-bed employed at Freiberg has already been described on p. 43.

At Fahlun, galena mixed with copper and iron pyrites and containing 6 to 10 per cent. of lead is roasted in quantities of 78 tons in ordinary stalls 13 to 16 feet long, 9 to 12 feet broad, and 3 to 6 feet high, 3 to 4 weeks being required. Coal is mixed with it to decompose the zinc sulphate, and the 78 tons of ore require 300 cubic feet of wood.

Roasting in Shaft Furnaces

Shaft furnaces are only employed for roasting purposes in the case of pyritic galena or galena containing pyrites and zinc blende, when the gases are to be used for making sulphuric acid or must be rendered harmless. The ores must not be too rich in lead, otherwise partial fusion is apt to occur.

If the ore is in lumps, kilns are employed. Pyrites burners are less serviceable for this purpose, because, on account of their lesser height, the layer of ore is not sufficiently deep to secure a high enough temperature for complete roasting.

Ores in the state of powder are roasted in dust furnaces (*schüttofen*), shelf furnaces not being employed for lead ores.

The roasting of the ores in shaft furnaces, though consuming very little fuel as the temperature is maintained by the burning of the sulphur, involves a large expenditure for labour, and suffers especially from the disadvantage of not being able to effect a thorough roasting, the operation having consequently to be followed by a second roasting in heaps or stalls, or in reverberatory furnaces for the small ore. Pyritic ores are roasted in kilns at Oker and at Freiberg.

At Oker, the ores containing 11 per cent. galena, 15 per cent. copper pyrites, 28 per cent. zinc blende, 25 per cent. iron pyrites, 14

per cent. heavy spar, and 7 per cent. of gangue, are first broken into pieces from 2 to 2½ inches square by a stone breaker, and then roasted in kilns until the sulphur content reaches 10 to 12 per cent. The construction of the kilns has already been described on page 51. Each kiln roasts 1·8 to 2 tons of ore in 24 hours. The roasted ores undergo two roastings, in heaps of 150 to 200 tons, the sulphur content being thereby reduced to 6 or 7 per cent. The first roasting occupies 4, and the second 3 weeks.

At Freiberg, pyritic lead ores are also roasted in kilns, the construction being shown on page 50. One and a half tons of ore are treated in 24 hours. The roasted ores mixed with others are again roasted in reverberatory furnaces.

At Freiberg, finely divided ore is roasted in the Gerstenhöfer furnace. The Gerstenhöfer furnace has been described and illustrated on page 52. Ores containing over 20 per cent. of lead are difficult to roast in dust furnaces on account of their readily sintering together.

At Freiberg, ores, containing 18 per cent. of galena, 60 per cent. of pyrites, and 22 per cent. of gangue, are first roasted in Gerstenhöfer furnaces 12 feet high, 4 feet 6 inches wide and deep, having 15 rows of fireclay bearers placed alternately six and seven in each row. In these the sulphur is reduced to 6 or 7 per cent., and then a further roasting in reverberatory furnaces follows, unroasted ore being mixed with half as much roasted ore in order to avoid sintering. Each furnace roasts 1·2 tons of ore in 24 hours.

At Oker, a form of muffle furnace (the Hasenclever furnace described on page 83) is used for roasting pulverulent ore of the composition given above.

Roasting in Reverberatory Furnaces

The furnaces employed are ordinary reverberatory furnaces, externally fired shaft furnaces not being used for roasting lead ores. The Stetefeldt shaft furnace, which has proved to be excellent for the chloridising roasting of silver ores, is of little service in the oxidising roasting of lead ores, because the time occupied by the ore in falling through the furnace is too short to effect a thorough oxidation.

Reverberatory furnaces with stationary hearths are preferable to those in which the hearth is kept in motion. The latter are only used for dust roasting and have to be worked in connection with stationary furnaces when it is necessary to sinter or fuse the charge

They are seldom used and only in places where the price of labour is excessive; in England they have been abandoned as unsuccessful.

The reverberatory furnaces used for roasting are connected with dust chambers for collecting the fume and the dust which is carried over mechanically. These are of special importance where the roasting charge is fused at the end of the operation as, in consequence of the high temperature prevailing near the firebridge, volatilisation of the lead, which is formed by the interaction of oxide, sulphate and sulphide, readily takes place.

Reverberatory furnaces with fixed hearths are of two kinds, those which are worked by hand and those worked by machinery. The latter are only occasionally used where the price of labour is high and have to be worked in connection with a reverberatory melting furnace when it is necessary to sinter or fuse the charge.

Furnaces worked by hand may also be divided into two classes; in the one worked discontinuously the ore is charged in all at once, and the whole of this charge is withdrawn at the conclusion of the roasting; in the other (the long-bedded calciner or *fortschaufelungs* furnace) the work is carried on continuously. In the latter form of furnace, which has a very long hearth, the ore is first charged in at the coolest end (nearest the flue) and is moved along at intervals, so that by the time it reaches the firebridge end the roasting is complete. This form of furnace is the one which is most in use and, as the older form is rapidly going out of use on account of its excessive expenditure in fuel and wages, it will not be further considered.

As in the roasting of copper ores, so in roasting lead ores, the *fortschaufelungs* furnace usually used has a single long hearth and working doors in each of the longer sides. Furnaces with two hearths one above the other are only used when it is absolutely necessary to economise floor space as the upper hearth is awkward to work, the roasting in it is incomplete, and repairs to either hearth necessitate the stoppage of the entire furnace.

If the roasted mass has to be melted together at the conclusion of the roasting (*schlackenröstung*), either a shallow depression or well is formed in the end of the bed nearest the firebridge, or else the level bed of the furnace at that end is placed in communication with a reverberatory melting-furnace by a perpendicular or inclined channel, the hot gases from this furnace passing over the hearth of the roasting furnace and out by the flue at the end. In Europe the well or sump at the firebridge end is used, whilst in America, and in most of the smelting works of the West, a special melting furnace is attached to the roasting furnace. This latter

arrangement, first introduced in Colorado, has an advantage over the former, in that it allows of the charge being kept in a pulverulent condition over the whole length of the hearth, so that it can be easily stirred up and a thorough roasting ensured, the rise of temperature requisite for fusion only taking place rapidly on the hearth of the melting furnace. In furnaces provided with a well, the charge which is on its way to that end of the furnace begins to soften and become pasty when it reaches the third or fourth working opening from the well, consequently thorough mixing of the mass and complete roasting is rendered impossible. In order to avoid this the heat is concentrated on the well as far as possible, and the mass just in front of it agglomerated and then melted down. The molten charge is tapped out of the sump or run out of the melting furnace, and is drawn out through the working doors when it is in a viscous condition.

The ore is usually charged into the furnace through an opening in the roof.

The length of the hearth including the well, but exclusive of the melting furnace, varies according to the amount of sulphur in the ore from 40 to 64 feet. With rich non-pyritic ores a length of 40 to 43 feet is sufficient, whilst with poor ores rich in pyrites it is extended to 60 or 64 feet, the pyrites furnishing some of the necessary heat. A greater length than this is useless, only increasing the first cost and the working expenses without a corresponding improvement in the roasting.

The hearth is made as broad as possible, as thereby the capacity of the furnace is increased, but it must not be made so broad as to interfere with proper working of the charge. It should not be less than 10 feet nor more than 16, the inside measurement in the United States furnaces being from 13 feet 9 inches to 16 feet.

The height of the roof of the working chamber is usually 16 to 24 inches and, in order to better utilise the heat, the roof is often made to slope slightly down to the end nearest the flue, or in some cases, the hearth itself rises somewhat towards the flue-bridge, either uniformly or in 3 or 4 steps of 3 inches in height. The hearth bottom is made of common brick, except in the neighbourhood of the firebridge, where firebrick is used, the well for the reception of the fused material and the hearth of the melting furnace being also best made of firebrick. As the furnace is cooled by the working doors on each of its long sides these should be as few as possible. They must be spaced so as to allow of the charge being moved readily, the distance between adjoining openings being not less than

6 feet nor more than 8 feet. The brickwork between the working door should project into the furnace as little as possible, and the working openings themselves are provided with doors of cast or sheet iron.

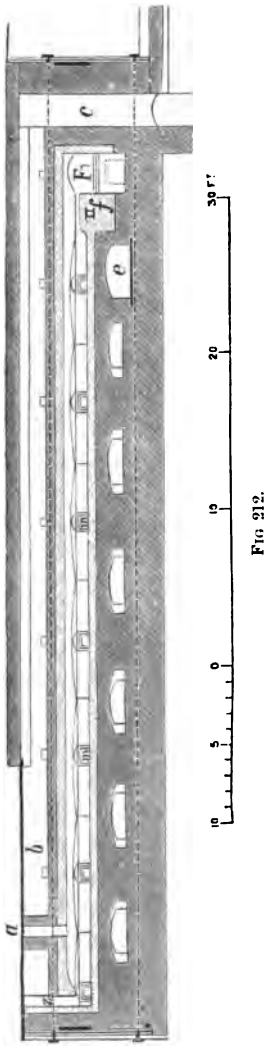


FIG. 212.

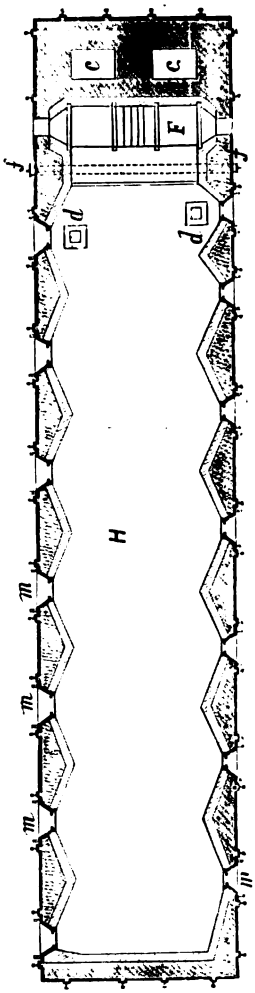


FIG. 213.

The amount of ore which can be roasted in a long-bedded calciner in 24 hours depends upon the character of the substances mixed with the ore, the size of the furnace, and the manner of roasting—whether the product is to be obtained in the pulverulent,

sintered or melted condition. Pyritic ores are more quickly roasted than those containing blende. The amount varies from 4 to 15 tons in 24 hours, and the consumption of fuel from 15 to 30 per cent. of the weight of the ore, depending upon the character of the coal employed and the manner of roasting. The time taken to work off a charge is from 2 to 6 hours, being dependent upon the nature of the ore and the form in which the product is to be obtained; if in a pulverulent form the time required is shorter than if the charge is to be melted. A furnace of average size working on good ores should turn out three charges in an eight hours' shift.

The percentage of lead in the ores treated in the roasting furnace varies within wide limits. In Europe it is fairly high, seldom amounting to less than 50 per cent., whilst in America argentiferous lead ores with less than 9 per cent. of lead are worked, the lead in this case serving as a solvent for the silver in the silver ore.

The construction of a *fortschaufelungs* furnace, in use at Przibram in Bohemia, with flat bottom and without a well in front of the fire bridge, is shown in Figs. 212 to 214.

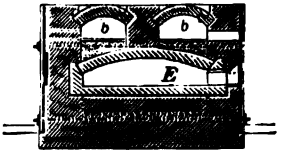


FIG. 214.

E is the heating chamber, F the fire-place, *f* the hollow water- or air-cooled firebridge, H the hearth, 47 feet 6 inches long and 8 feet broad. The ore is introduced in charges of 1 ton through an opening *a* which can be closed at will, situated in the roof of the furnace near the flue-bridge, and is then gradually worked along towards the firebridge. Arriving there it can be withdrawn through the two last working-doors or can be raked through the perpendicular openings *d* in the hearth ordinarily closed by bricks; *m m* are the working doors. The hot gases from the fire pass along the entire length of the working space, and after leaving it by the flue *z*, pass along the top of the furnace through the flues *b*, *b* to the passage *c* leading into the stack.

As soon as a roasted charge is withdrawn from the furnace (1 ton every 6 hours) the charges which are lying in front of each working door are each in turn moved a step nearer to the firebridge and a fresh charge introduced at the other end of the furnace.

In a furnace of this kind seven separate lots of ore of 1 ton each are undergoing roasting at one time, the ore containing 51 to 58 per cent. of galena, 8 to 11 per cent. of zinc blende, and 12 to 14 per cent. of silica, and the roasted mass only 1 per cent. of sulphur. Every six hours one lot (of 1 ton) is withdrawn, so that 4 tons of ore are

worked in 24 hours. A mixture of lignite and ordinary coal is used as fuel, and the consumption varies from 35 to 38 per cent. of the weight of the ore roasted.

Figs. 215 to 217 illustrate a form of furnace with a well in front of the firebridge in use at the Mulden Works at Freiberg.

A is the heating space, *f* the hollow air-cooled firebridge, H the hearth 42 feet 6 inches long and 10 feet 8 inches broad, which rests on cast iron plates in order to prevent any of the molten roasted charge from trickling through. The grate is divided by means of a hollow air-cooled wall *p* into two portions, each being fired independently of the other. The air enters the hollow wall *p* at *w* and passes through openings in it partly over and partly behind the firebridge; *z*, *z*, *z*, are working doors, of which there are ten on each of the two longer sides of the furnace. S is the well, and *y* the door through which the viscid roasted mass is drawn out into iron wagons. The hot gases from the furnace pass through the flue M on their way to the system of condensing flues and thence into the stack. The charge is introduced into the furnace through the opening *x* in the roof.

This furnace usually holds 5 charges at one time, each weighing 1½ ton. The charge consists of a mixture of various kinds of ore, which have undergone a previous roasting in shaft furnaces, lead ores proper, silver and copper ores, pyritic ores and those containing blende. On an average the mass to be roasted contains 20 to 30 per cent. of lead, 20 per cent of sulphur, not more than 10 per cent. of zinc, and 20 to 25 per cent. of silica. Every three hours a charge is withdrawn from the furnace, so that 12 tons of ore are roasted in 24 hours, the sulphur content of the roasted ore being 3 to 4 per cent. This amount of sulphur must be left in on account of the copper present with which it has to combine in the smelting process. The coal used amounts to 25 per cent. of the weight of the charge, and six workmen are required for each furnace.

Reverberatory furnaces with two hearths placed one over the other are used at Mechernich (Rhenish Prussia). The hearths are each 48 feet 9 inches long and 13 feet broad, and there are working doors on each of the longer sides of the furnace. One furnace roasts 9 tons of ore containing 50 to 60 per cent. of lead and about 20 per cent. of silica every 24 hours, 15 per cent. by weight of coal being used.

Figs. 218 to 223 show the arrangement of a roasting furnace, to which is attached a special furnace for melting the charge, such as is

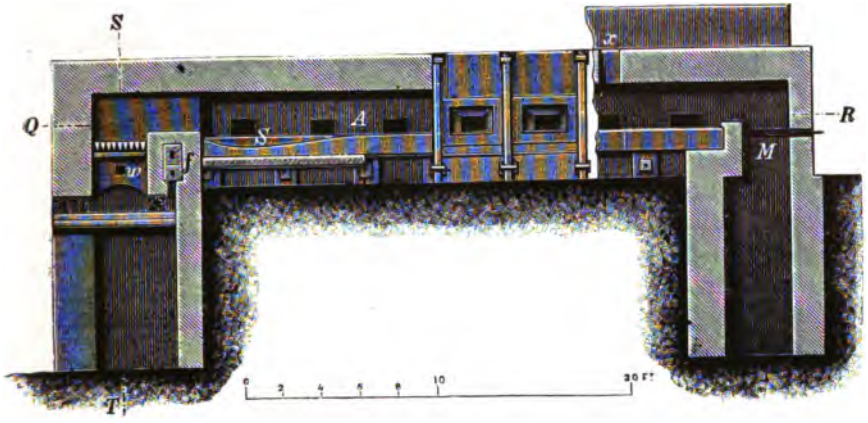


FIG. 215.

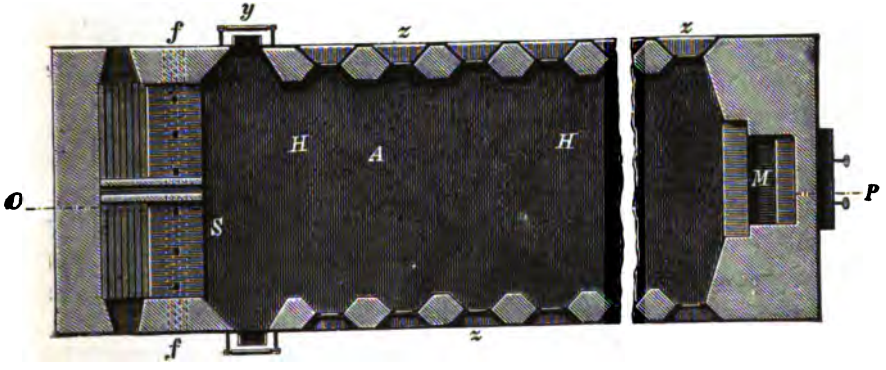


FIG. 216.

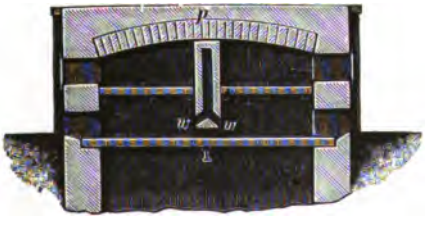


FIG. 217.

employed in the Western States in America. The hearth (exclusive of the melting hearth) is 60 feet long and 13 feet 9 inches broad. The fireplace is placed at the end of the melting furnace. The flames pass first over the melting hearth and then ascend through a perpendicular slot at the end into the roasting furnace, passing along its entire length, and then through the flue into the dust chambers and away to the stack. The hearth bottom is divided into four terraces rising towards the flue end, each division being 3 inches higher than the one below it. The furnace roof is composed of fire-brick, except the portion over the last division of the hearth, which is of common brick. The hearth of the melting furnace is made of a fire-resisting stone, quartz linings not having proved successful, and it is supported on two masonry arches, which allow the air to cool it underneath. The charge is introduced through a hole in the furnace roof close to the flue bridge. The molten mass is drawn out of the furnace into slag pots and is broken up after cooling.

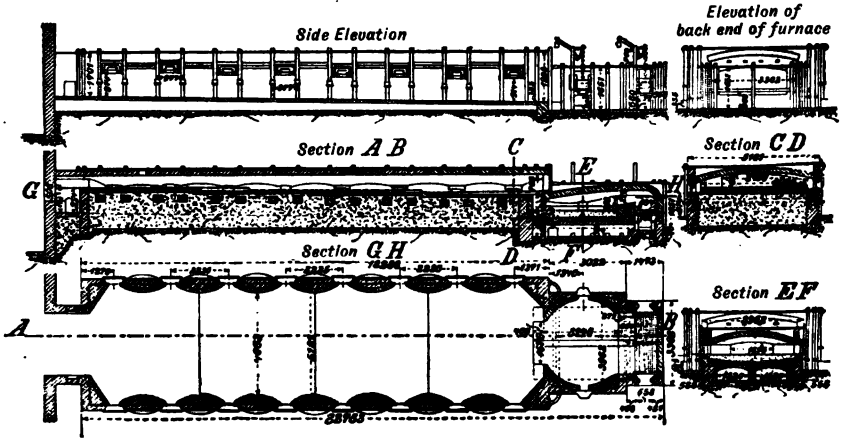
Such a furnace will roast and melt six to eight charges of ore, each weighing one to one and a half ton, in 24 hours (6 to 12 tons in all), with a consumption of 25 to 30 per cent. of coal. Three men are required, one to attend to the firing and the melting furnace, the other two working the roasting furnace.

At the time of the author's visit to the Omaha and Grant Smelting Works, at Denver, Colorado, U.S., a furnace of this kind was roasting and melting 11 tons of ore in 24 hours, the ores containing 14 per cent. of lead with 60 to 75 ounces of silver per ton, 7 to 10 per cent. of zinc, 30 to 40 per cent. of iron, and 30 per cent. of silica. The product contained 8 per cent. of sulphur; 3 tons of coal were used, and the labour of three men was required.

The working of the roasting furnace is conducted as follows: the ore is spread on the hearth in a layer about 2 inches thick, and as soon as it attains a dull red heat it is stirred from time to time, so as to expose every portion of it to the action of the air. When one of the charges corresponding to $\frac{1}{2}$ to $1\frac{1}{2}$ tons of ore is drawn out of the furnace, all the other charges are turned and raked over and moved along towards the firebridge, the one vacant space thus left at the end of the furnace receiving a fresh charge of ore. The drawing of the finished charge and the introduction of the fresh one take place at intervals of from $2\frac{1}{2}$ to 6 hours, the time depending on the nature of the ores, pyritic ores roasting more quickly than ores containing blende.

During their passage from the flue-bridge to the firebridge the charges are subjected to a gradually increasing temperature. If it is

desirable to melt the charge, and the furnace has not a melting furnace in connection with it, the charge, as it arrives at the firebridge, is heaped up in the well and there melted down. If there is a melting furnace, then the charge lying on the hottest part of the hearth is pushed down on to the hearth of the former and there melted, some quartzose ore being usually first sprinkled on the hearth in order to protect it. As soon as the surface begins to show signs of fusion the whole mass must be stirred up so as to expose the bottom portions; the stirring need only take place at first at half-hourly intervals, but after a time the mass must be stirred every five or ten minutes. As soon as the charge is melted it is drawn out into slag pots or other forms of iron vessel.



FIGS. 218—223.
Dimensions in Millimetres.

When the roasted charge is to be melted, additions of iron oxide or iron refinery slags are often made which render the mass easily fusible, and facilitate the subsequent smelting in the blast furnace. In those cases where the charge is only to be sintered together (*sinterrösten*) or to be left in a pulverulent state (*staubrösten*), the temperature of the furnace at the firebridge end is kept correspondingly lower.

The output of the various forms of reverberatory roasting furnace varies from 4 to 15 tons in the 24 hours, the amount depending on the materials present in the ore, the manner of roasting, the number of workmen, and the character of the fuel.

The essential constituents of various ores after they have been subjected to slagging-roasting and sinter-roasting are shown in the following table:—

Constituents.	Ore after slagging-roasting (*Schlackenröstung*).		Ore after sinter-roasting (*Sinterröstung*).	
	Freiberg.	Mechernich.	Rodna (Transylvania).	Hall Valley (Colorado).
Pb	—	62·08	54·27	—
PbO	22	—	—	42·04
Ag	0·13	—	0·061	Ag_2O=0·21
Au	—	—	0·0001	—
Cu	—	0·14	0·02	—
Cu_2O	0·3	—	—	—
CuO	—	—	—	1·71
As	—	—	0·03	—
As_2O_5	1·1	—	—	—
Sb	—	0·08	0·027	—
Fe	—	0·56	24·06	—
FeO	—	—	—	3·59
Fe_2O_3	33·3	—	—	—
Zn	16	—	0·87	—
ZnO	—	—	—	—
Al_2O_3	1·8	4·24	0·23	8·11
CaO	2·0	1·18	—	—
MgO	0·5	—	—	0·42
BaO	—	—	—	12·05
SiO_2	17·4	22·77	0·80	22·71
CO_2	—	—	—	—
SO_3	traces	—	2·25	6·31
S	3·6	0·60	2·72	2·94
O	—	—	13·41	—

Roasting furnaces, with a fixed working chamber, but in which the stirring and moving of the charge is effected with the aid of machinery, are only very exceptionally used.

At the Globe Smelting Works, Denver, Colorado, at the time of the author's visit (May, 1892), the O'Harra furnace described on page 72 was in use for roasting lead ores. A melting furnace was worked in conjunction with it, but the author is not acquainted with the results obtained.

The employment of such furnaces with their very large working capacity for the roasting of lead ores would be a distinct advance, but only those ores could be employed which would not easily fuse or frit together, such as pyritic ores or ores containing zinc blende which are at the same time poor in lead.

Reverberatory Furnaces with Movable Hearths (Rotating Cylinders)

These are only rarely used, and only when the roasted ores are to be turned out in the pulverulent state, the sintering or melting of the charge having to be performed in a special melting furnace. Whilst the roasting of ores which do not sinter can be readily con-

ducted in such furnaces at uniform temperatures, ores which sinter can only be roasted up to a certain point and not completely.

With ores which roast slowly (those containing blende) a repetition of the roasting in one of the furnaces previously mentioned is necessary. The combination of a melting furnace with a furnace of this description has in most cases proved unsatisfactory.[1]

Brückner's cylindrical calciner (see page 80), in which the roasting can be better controlled owing to its intermittent working, has proved better adapted for roasting ores which do not sinter than the continuously working calciners of White, Howell, Hocking and Oxland (see page 81).

For roasting lead ores in Utah, Brückner proposed an arrangement of several cylinders one over the other with a melting furnace placed in connection with the lowest[2]; this system, however, has not yet been carried out.[3]

At Spezzia, a Brückner furnace is said to be used in conjunction with a melting furnace for roasting lead ores. Gas firing is employed, and the air for burning the gas is heated; by periodically reversing the gas current a uniform temperature can be maintained.[4] The author is not acquainted with the result of this arrangement.

For rich lead ores, the reverberatory furnace with a fixed working chamber is in all cases to be preferred to the rotating cylinder. The use of the latter is limited to those cases where the ores are poor in lead, not easily sintered, and mixed with blende or pyrites, and where labour is costly.

Exact information with regard to the technical and economic success of these furnaces is so far wanting.

The Smelting of the Roasted Ores in Shaft Furnaces (*Reductionsarbeit*)

Roasted lead ores which have been completely calcined in reverberatory furnaces and then melted up with silica (*schlackenröstung*) contain their lead as oxide and silicate. If the roasting which precedes the melting has been incomplete, as is the case for instance when there is a sufficient amount of copper present to make its extraction profitable, unaltered lead sulphide will also be present. In all other methods of roasting, the roasted ores contain lead sulphate as well as oxide and unaltered sulphide.

The foreign substances present in the roasted ores are usually oxides, sulphates and sulphides of iron, zinc, copper and compounds of

[1] *Trans. A.I.M.E.* x. p. 42.
[2] *Eng. and Mining Journal*, Jan. 15, 1887
[3] Terhune, *Trans. A.I.M.E.* xvi. p. 20.
[4] *Eng. and Mining Journal*, Dec. 20, 1884.

arsenic and antimony, especially arseniates and antimoniates, quartz, silicates, lime, magnesia, and barium and calcium sulphates.

These roasted ores are then smelted in shaft furnaces with carbonaceous fuel, and with ferruginous materials and other suitable fluxes, in order to obtain the lead in the metallic state, to convert the copper, if present in sufficient quantity, into a regulus or matte, to collect any silver or gold present in the lead produced (partly in the matte), and to volatilise or to slag off the other bodies.

The lead is reduced from the compounds which are present in the following ways. Such lead oxide as is present in a porous condition is reduced to metal by the carbon monoxide existing in the upper regions of the furnace; if the mass is sintered or melted together the carbon monoxide is unable to penetrate to the interior, and in such cases the reduction of the oxide is effected by contact with the hot solid carbon in the lower portions of the furnace.

Carbon monoxide alone cannot reduce lead silicate, and basic lead silicates only yield a portion of their lead, being converted into difficultly fusible acid silicates or mixtures of free silica and lead silicate. Lead which is present as silicate is accordingly set free by the combined action of ferrous oxide and carbon, the ferrous oxide converting the lead into oxide, and being itself converted into silicate, and the oxide thus produced being then reduced by the carbon. The requisite ferrous oxide is either formed in the furnace by the reduction of ferric oxide by carbon monoxide, or is added as a ferruginous slag containing excess of ferrous oxide, or else it is produced from ferrous silicates by the action of lime. The reduction of the lead is accordingly effected either by ferric oxide and carbon, or by carbon and slags containing ferrous oxide in excess, or by a ferrous slag, lime and carbon, the lime being added to the charge in the form of limestone. Lead is only reduced from its silicate by carbon and lime alone, without ferrous silicate, at a very high temperature.

Lead is also reduced from the silicate in small quantities in the hottest portions of the furnace by metallic iron produced by the reduction of the ferruginous material added, the iron forming ferrous silicate.

Possibly also sulphides of iron, barium and calcium reduce some of the lead silicate in the hotter regions of the furnace forming sulphur dioxide and silicates of the metals. Sulphide of iron may be present owing to imperfect roasting of the ore, or may be produced by the reduction of galena by metallic iron, or by the action of galena on basic iron silicate in presence of carbon thus:—

$$Fe_4SiO_6 + 2PbS + 2C = Fe_2SiO_4 + 2FeS + 2Pb + 2CO.$$

whilst calcium and barium sulphides are formed by the reduction of their sulphates by carbon.

The lead sulphide present in the charge owing to imperfect roasting, or formed in the furnace by the reduction of lead sulphate, is mainly reduced to metal in the hotter parts of the furnace, either by metallic iron formed by the reduction of ferric or ferrous oxides by carbon, or by basic iron silicates and carbon, iron sulphide being produced at the same time. The iron sulphide finds its way into the lead matte (*bleistein*).

A certain quantity of lead is also produced when the charge becomes pasty by the interaction of oxide and sulphate, which have escaped reduction with unaltered lead sulphide.

Lime and carbon are also able to partially reduce lead sulphide in the lower portions of the furnace according to the equation (after Berthier):—

$$2PbS + CaO + C = Pb + PbS{\cdot}CaS + CO.$$

Lastly, zinc vapour, formed by the reducing action of carbon upon zinc oxide contained in the charge, is able to decompose lead sulphide producing metallic lead and zinc sulphide (Percy and Smith). The reasons for the addition of ferruginous materials and carbon to the charge will be clear from a consideration of the above reactions.

Lead sulphate is decomposed in various ways in the furnace. The greater part of it is reduced by carbon to sulphide in the lower portions of the furnace, this sulphide being subsequently reduced to metal in one of the ways mentioned. Another portion reacts with lead sulphide as soon as the charge becomes pasty, producing lead and sulphur dioxide, and a third portion may form lead silicate in presence of free silica or acid silicates, this being in turn reduced as previously shown.

Ferruginous and carbonaceous materials are accordingly necessary for the production of the metal from its sulphate.

Amongst the other substances contained in the roasted ores the oxide of iron is, as already mentioned, reduced by carbon to ferrous oxide which combines with silica, a portion, however, being reduced to metallic iron, which is required for the decomposition of lead sulphide and the separation of the lead contained in it.

Ferrous sulphate is decomposed in the furnace into ferric oxide and sulphur trioxide, or sulphur dioxide and oxygen, the ferric oxide thus set free being reduced to the ferrous state and then passing into the slag.

Ferrous sulphide partly reacts with lead silicate in the manner previously mentioned, and is partly dissolved by the slag. If present

in larger proportions it combines with a portion of the still undecomposed sulphide of lead, forming a lead matte, or if copper sulphide is present, a cupriferous matte or regulus.

The behaviour of zinc oxide and sulphide in the smelting process and the injurious effects of these substance have already been considered on pages 320 and 321.

Zinc oxide is dissolved by highly ferruginous slags, this being the more easily effected the richer the slags are in iron. As the reduction of zinc oxide to zinc is undesirable owing to the injurious action of the zinc vapour on the process (except in those cases where white pigments are prepared from the flue dust) the zinc is as far as possible induced to pass into the slag by keeping the furnace temperature fairly low and having a highly ferruginous easily fusible slag. As before mentioned, zinc vapour is partially oxidised by carbon dioxide and water vapour, and gives rise to deposits of *furnace calamine* on the sides of the furnace. A portion of the zinc may also be converted by carbon and sulphur dioxide into zinc sulphide, which is also deposited in the solid state on the furnace walls.

Any zinc sulphide which may be present in the charge behaves much more deleteriously than the oxide, as it is only taken up by the slag in small quantities, rendering the latter very thickly fluid. If a regulus or matte is being produced, a portion of the sulphide finds its way into that and renders it also difficultly fusible. In many cases the presence of zinc sulphides renders the separation of the regulus from the slag impossible, a mixture of the two being obtained, known in Sweden as *skumnas*. Only a small proportion of the zinc sulphide is decomposed in the hottest portions of the furnace by iron, with formation of iron sulphide and zinc vapour.

Zinc sulphate is partly decomposed into oxide and sulphur trioxide, and partly reduced to sulphide.

Cuprous and cupric oxides are reduced to metal which then combines with sulphur, and together with iron and lead sulphides forms the regulus or matte. If the matte is only produced in small quantities it is absorbed by the slag, whilst in larger quantities it separates out from it. If there is no sulphur for the copper to combine with, it finds its way partly into the lead and partly goes into the slag. Copper sulphide, present as such in the roasted ore, combines with iron and lead sulphides, and also with a part of the zinc sulphide to form a regulus. Copper sulphate is partly reduced to sulphide and partly decomposed into oxide and sulphur trioxide.

Arseniates are partially reduced to metallic arsenic, losing also a portion of their arsenic by volatilisation. To a certain extent the

arsenic goes into the slag and into the regulus, whilst if present in large amounts it gives rise to the formation of a speiss, carrying with it part of the lead and silver, the chief metal in the speiss being, however, iron. Small quantities of arsenic will also be taken up by the lead.

Antimoniates are partially reduced to metallic antimony, whilst a portion of the metal is volatilised. The antimony alloys with the lead, but can also contribute to the formation of a speiss if copper be present, or mix with the arsenical speiss if one be formed. Antimony sulphide is decomposed by metallic iron, ferrous sulphide being produced, the separated antimony alloying with the lead.

Any gold or silver present in the roasted ores is taken up by the lead. In cases where a regulus or a speiss is formed, a portion of the precious metals would also be found in them.

Any manganese oxide present is reduced to manganous oxide and goes into the slag. The latter is rendered very fusible by the manganous silicate, but may thereby lose its power of absorbing zinc oxide, magnesia, and barium sulphide.[1]

Lime goes into the slag and is able to replace part of the ferrous oxide in it, so that an addition of lime (in the form of limestone) to the charge permits of the employment of a smaller quantity of ferruginous material. The proportion of lime added, however, must not be excessive, although it leads to a diminution in the specific the slag, because it renders the latter less fusible and thus necessitates the employment of an increased amount of fuel. The greater the proportion of lime replaced by iron in the slag the better the working of the furnace.

When the charge does not contain any zinc, the percentage of lime present in the slag must not exceed 30 per cent., whereas, if zinc be present, the amount of lime must be kept as small as possible, as the more iron the slag contains the more easily it will take up the zinc compounds.

With high percentages of lime (28 per cent.) in the slag it practically ceases to absorb zinc. In American practice,[2] if the charge contains 9 or 10 per cent. of zinc, it is not considered advisable to have more than 16 per cent. of lime in the slag.

Magnesia passes into the slag in the same manner as lime. It renders the slag very refractory, and any considerable percentage is to be avoided if zinc be also present, so small a quantity as 5 per cent. interfering with the successful working of the furnace.[3]

[1] Hofman, *The Metallurgy of Lead.* [2] *Ibid.*, p. 141.
[3] Hofman, *op. cit.*

Fluor spar is very fusible, and possesses the power of readily fluxing difficultly fusible substances, especially heavy spar and gypsum.

Silicates and quartz pass into the slag, bases or basic silicates being added to serve as fluxes for acid silicates, whilst basic silicates require siliceous additions.

Heavy spar is partly reduced to barium sulphide, partly converted into barium silicate by the action of silica and ferrous sulphide, or of silica and iron, the barium silicate combining with the resulting ferrous silicate and going into the slag. If a regulus or matte is being produced, a small amount of the barium sulphide passes into it, but if not, then the whole of the sulphide goes into the slag.

Calcium sulphate behaves similarly to the barium salt, calcium sulphide being soluble in the slags, particularly if they are rich in lime.

In order to properly carry out the reactions which have just been considered, and in order to ensure a complete separation of the lead produced, from any regulus or speiss which may be formed, the ingredients in the charge must be so proportioned that a readily fusible slag is produced, not too heavy, and containing its silica as a monosilicate or nearly in that proportion, the base being chiefly iron with a small amount of lime. If large amounts of zinc are present the slag will have to approximate to a subsilicate or be between that and a monosilicate, the amount of iron increasing with the amount of zinc oxide and alumina present. If alumina is present in smaller quantities, then the slag may be a mixture of mono- and bi-silicates, forming the so-called sesquisilicate.

Siliceous ores require the addition of basic materials, and ores containing large amounts of iron require correspondingly large additions of siliceous ores, acid silicates or slags. Basic iron slags, roasted lead matte, red and brown hæmatite, burnt pyrites may all be employed where basic ferruginous materials are indicated. Limestone in smaller quantities may also be employed as a basic addition, because as already mentioned, it sets free ferrous oxide from basic iron slags in the presence of lead silicate, ferrous silicate being formed at the same time.

Slags from the same process, provided they are fairly free from zinc, may be used as a flux to prevent the choking of the furnace by pulverulent ore; slags from the working up of the regulus can be used for the same purposes.

It is not advisable to introduce more than 36 per cent. of silica

into the slag. With 40 per cent. the slag begins to be refractory, and the furnace consequently requires more fuel.

With still larger amounts of silica the furnace yield falls off, lead passes into the slag and is also volatilised, and, as shown on page 89 (see copper), metallic iron may be reduced from the slag and give rise to the formation of furnace "bears."

If the percentage of zinc present is not very great, it is not advisable to have less than 27 or 28 per cent. of silica in the slag, as otherwise large additions of ferruginous material are necessary, and then there is a risk of the reduction of metallic iron from the slag. In addition to this danger, highly ferruginous slags are difficult to separate from the lead, and particularly from the matte. With a large amount of zinc present, then the percentage of silica may be considerably reduced.

If heavy spar be present at the same time, the silica content may be reduced to as little as 15 per cent. without the slag losing the properties which it must possess for successful working. The most satisfactory proportion of silica in the slag lies between 27 and 36 per cent.

The amount of lime present in the slag, as already shown on page 343, should not exceed 30 per cent. with ores which are free from zinc, as otherwise the slag becomes too refractory, requiring in consequence a larger amount of fuel and enhancing the risk of the reduction of metallic iron owing to the higher working temperature. In the case of zinciferous ores the lime must be kept low, as zinc will not pass into the slag if it contains more than 28 per cent. of lime.

In Europe the addition of lime in the roasting and reduction process is never practised, or only to a very slight extent, but in America considerable amounts of lime in the form of limestone are employed, owing to the comparatively high price of ferruginous materials.

The proportion of ferrous oxide in the slag should not exceed 50 per cent., as otherwise there is a danger of iron being reduced and the specific gravity of the slag becoming too high. On the other hand, the percentage should not fall below 24, as the earthy bases, which in such cases must take the place of the iron, render the slag too refractory.

The relative proportions of silica, ferrous oxide and lime, which have been found most suitable in various American smelting works, are given in the following table, the authority being given in each case. It must be understood however that the slags are not exclu-

sively those of the roasting and reduction process, but include some formed by direct smelting of carbonate and sulphide ores.

Metallurgist.	Silica per cent.	Ferrous and manganous oxides per cent.	Lime (baryta, magnesia) per cent.	Total, exclusive of alumina, zinc oxide, and similar bodies.
Eilers	28	50	12	90
Eilers	30	40	20	90
Schneider	33	33	24	90
Rath	35	27	28	90
Hahn	34	50	12	96
Page	33	36	16	85
Livingstone	30	36	20	86
Hahn	36	40	20	96
Iles	32	33	23	88
Murray	40	34	26	100

The composition of various European slags from the roasting and reduction process is given in the following table :—

	From Freiberg in Saxony.		
	Old Slags.		Slags from recent working.
	1	2	
Silica	28·14	27·05	27·2
Ferrous oxide	37·23	41·21	40·1
Zinc oxide	7·60	8·62	10·1
Lead oxide	7·35	3·90	5·7
Copper oxide	0·50	1·00	not estimated.
Alumina	5·78	6·85	
Lime	7·68	8·84	
Baryta	3·87	—	
Magnesia	0·63	0·90	
Sulphur	2·47	3·53	

	Freiberg. Muldener Hütte, recent analysis.	Braubach.	Altenau.	Mechernich.		Przibram.	Lower Harz. Julius- and Sophien-Hütte.	
				1.	2.		1.	2.
SiO_2	23·95	27·85	30·32	35·05	31·27	37·50	16·90	13·64
FeO	44·41	39·03	35·72	20·89	32·64	28·37	35·05	not estimated
MnO	0·92	4·74	—	2·23	1·24	2·51	—	—
CaO	4·75	13·90	16·15	21·77	20·44	14·70	6·05	8·12
MgO	0·54	3·18	—	1·13	1·18	1·11	—	0·60
Al_2O_3	4·45	2·33	3·20	9·71	8·14	7·81	6·31	2·44
BaO	—	0·85	—	—	—	—	—	—
CuO	0·86	0·13 (Cu_2O)	0·18 (CuO)	—	—	—	—	0·85 (Cu)
PbO	2·87	0·29	1·13 (Pb)	1·0 (PbS)	1·13 (PbS)	0·48	—	1·17 (Pb)
ZnO	14·81	4·35	7·27	—	—	4·07	19·64	19·09
S	4·46	2·72	1·47	—	—	0·92	—	1·92
$BaSO_4$	—	—	0·19	—	—	—	10·24 (8·13 BaS)	19·23
Ag	—	—	0·0007	—	—	0·00125	—	—
Cu_2S	—	—	—	0·04	0·06	—	—	—
Sb_2S_3	—	—	0·009 (Sb)	—	0·14	—	—	—
P_2O_5	—	—	2·04	—	—	2·11	—	—
Fe_2S	—	—	—	4·95	2·94	—	—	—
K_2O+Na_2O	—	—	1·28	—	—	—	—	—

SLAG FROM LA PISE (FRANCE).

SiO_2	30	Al_2O_3 and MgO	5–6
FeO	40	Pb	2–3
CaO	20		

In successful working, the slag from the roasting and reduction process should not contain more than 0·5 per cent. of lead by dry assay, and not more than 0·5 ounce of silver per ton, assuming that the work lead does not carry more than 300 ounces per ton.

The fuel used is a carbonised fuel, either coke or charcoal, or a mixture of the two. Natural fuels are not generally used, as they undergo a coking in the upper parts of the furnace, altering in volume and leading to irregular working and volatilisation of lead. Anthracite is, however, employed to a certain extent in admixture with other materials in the United States.[1] As, according to the researches of Schertel,[2] the reduction of the lead in the roasted ore, when the latter has been melted or sintered, is chiefly brought about by contact with solid carbon, it is not essential that large quantities of carbon monoxide should be produced from the combustion of the carbon. It is therefore better to burn the carbon as far as possible to carbon dioxide, in order to obtain the greatest amount of heat from it. For this reason the less porous coke is to be preferred to the more porous charcoal, as carbon monoxide is less liable to be produced by its combustion. The temperature, however, must not be raised to such a degree as to volatilise large quantities of lead, and to reduce metallic iron from the oxide and silicate.

SMELTING FURNACES.

The smelting furnaces generally used are shaft-furnaces, which may be either draught furnaces or fed by an air-blast. The employment of draught furnaces is exceptional, and then only with easily fusible charges, the use of blast furnaces being the rule.

DRAUGHT FURNACES.

In draught furnaces the air is drawn into the furnace, either by means of a stack draught or with the aid of an exhauster.

Draught furnaces of the former type, or air shaft furnaces, were formerly employed in the Sierra de Carthagena (Spain), but are now mostly replaced by blast furnaces. These furnaces are connected by flues running up the hillsides, with a high stack. The air enters

[1] *Trans. A.I.M.E.*, xx.

[2] *Jahrbuch für das Berg-und Hüttenwesen im Konigreich Sachsen*, 1880.

the furnace through nozzles in its sides. As a high pressure cannot be obtained ($\frac{3}{16}$ of an inch of mercury at the most), the height of the column of material in the furnace must of necessity be small. The construction of such a furnace is shown in Fig. 224.

It will be seen that it is a crucible furnace with six clay tuyeres *l*, the upper portion being protected by a retaining wall. The furnace shaft terminates in the flue *v*, which connects it with the stack. The charge and fuel are introduced through the opening *e*, which can be closed by a door, in order not to interfere with the draught. The slag flows out through a hole into the slag-channel in the forehearth *d*, and the lead, which collects in the brasque crucible *b*, is

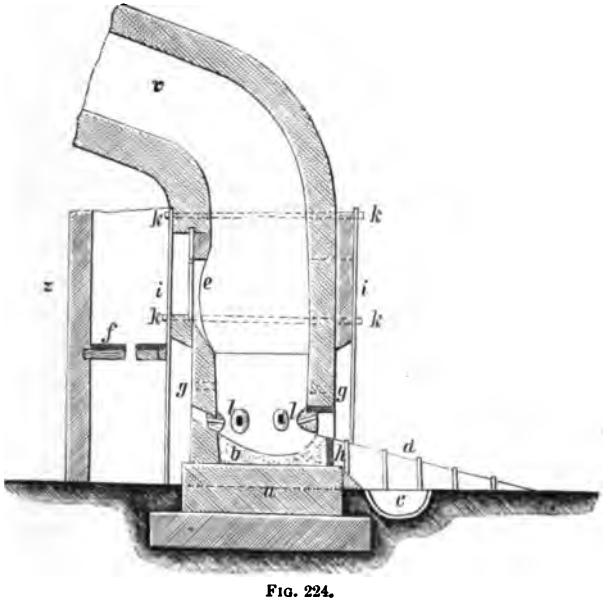


FIG. 224.

tapped out into the forehearth *c*. To ensure a uniform distribution of air to the tuyeres, a wall *z* is built round the lower portion of the furnace.

These furnaces can only be employed with easily fusible charges; they are extravagant in their consumption of fuel, and require careful attendance to prevent any irregularities in the draught from upsetting the working of the furnace. They can therefore only be employed under quite exceptional circumstances.

The Herbertz furnace is an example of furnaces of the second class, and has been tried experimentally for lead smelting.

In this furnace the necessary draught is obtained by a steam jet

placed in the furnace throat. The air is drawn in through an annular slot, which can be widened or narrowed, this being rendered possible by supporting the entire hearth on strong screws and raising

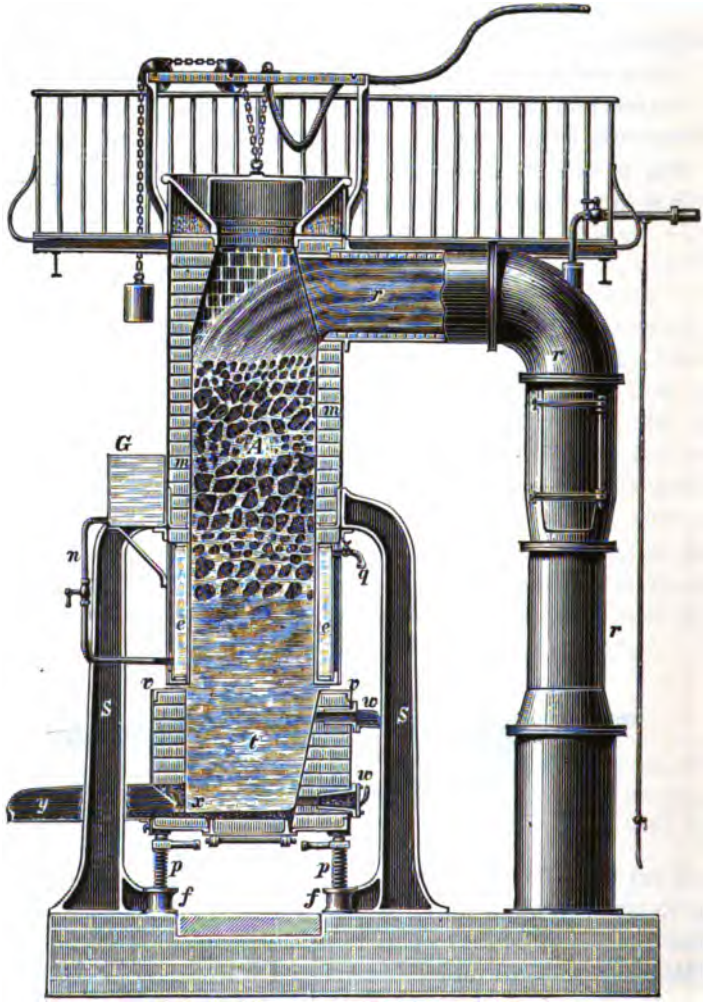


Fig. 225.

or lowering it. The construction of the furnace will be seen from Fig. 225. *A* is the shaft, the upper part of which *m* is, constructed of masonry, whilst the lower part above the crucible *t* is a hollow water-cooled iron cylinder. The upper part of the furnace is supported on the

columns *s*. Screws *p*, resting on iron feet *f*, carry the crucible of the furnace and permit of its being raised or lowered; *v* is the circular slot for the entrance of the air; *w w* are sight-holes; *x* is the tap-hole of the crucible, and *y* the running-off spout. The waste gases pass along the pipe *r* into condensing chambers. The cooling water for the hollow iron jacket passes from the cistern *g* by the tube *n* into the lower part of the jacket, passing away from the top by the tube *q*. The partial vacuum in the furnace, produced by steam at 4 or 5 atmospheres' pressure, amounts to $1\frac{1}{2}$ to $2\frac{1}{2}$ inches of mercury, measured 3 feet above the point of the entrance of the air.

These furnaces, which have answered well for melting pig-iron, have only been tried experimentally for lead smelting.

BLAST FURNACES

are chiefly employed in the smelting of lead ores, and have undergone extensive changes of recent years, particularly in the United States during the last decade.

The low blast furnaces (*krummöfen*) formerly employed, with all their attendant disadvantages—high fuel consumption, large loss of lead by volatilisation, small capacity and short life—are now replaced by much taller furnaces. Furnaces, square or trapezoidal, in horizontal section, are also being replaced by circular, elliptical or rectangular furnaces on account of their greater capacity.

Instead of the furnace body widening from the throat to the tuyeres (Vogel furnace), and having tuyeres on one side only, the furnaces now used contract downwards to the tuyeres, the latter being arranged symmetrically all round the furnace.

In the older form of furnace volatilisation of lead was avoided by maintaining a comparatively low temperature in the zone of fusion and a complete separation of the lead or of the matte from the slag was ensured, owing to the distance which the molten mass had to traverse from the tuyere to the front of the furnace. These advantages were more than counterbalanced by the incomplete reduction of lead from the slag and matte, in consequence of the low temperature in the crucible, and by the high velocity of the gases in the narrowed throat of the furnace, resulting in a very incomplete transference of their heat to the charge, and a large escape of lead fume and flue dust.

The furnaces, with a narrow crucible widening up to the throat, enable the lead to be more perfectly extracted from the slag owing to the higher temperature, loss of lead is to a certain extent pre-

vented, and the descending charge abstracts a larger proportion of the heat of the waste gases owing to their smaller velocity. The formation of furnace accretions is to a great extent prevented by the friction of the descending charge against the furnace walls. Occasionally the furnace is slightly narrowed again towards the throat, after widening below, in order to quickly carry off zinc vapour through a tube hung in the centre of the furnace top.

Furnaces, with easily accessible base and framework, built of light masonry or cased in boiler iron, or with the brickwork wholly or partially replaced by waterjackets, have superseded the older furnaces constructed of massive masonry and difficult of access.

The output has also been greatly increased by using larger furnaces, a greater number of tuyeres, and a greater amount, as well as a higher pressure of blast. The height of the furnace has a certain definite limit. If it is too low, then volatilisation and an incomplete transference of the heat of the waste gases to the charge occur; if too high, then iron is reduced from the charge. With charges rich in iron, lower furnaces are used than in those cases where the charge is rich in lime and silica.

With charcoal as fuel taller furnaces should be used than where coke is burnt, because with charcoal combustion rapidly spreads upwards, and consequently with a low furnace, a considerable portion of the fuel would be uselessly burnt at the throat. If the ores are rich in zinc the furnace must not be too high, as, if it is not possible to pass all the zinc into the slag, the volatilisation of part of it is aimed at, and with a high furnace this might lead to deposits of furnace calamine.

The distance from the tuyere level to the upper surface of the charge has an important influence on the output, and varies in modern furnaces from 10 to 18 feet. In the Freiberg Pilz furnace of circular section this distance is 17 feet 10 inches up to the flue level; in the Schemnitz Pilz furnace 11 feet 6 inches; in the new Pilz furnace at Friedrichshütte 12 feet 3 inches; in the rectangular Raschette furnace at Altenau in the Harz it is 16 feet 6 inches; and in the American furnaces of rectangular section 10 feet to 17 feet 10 inches. In the United States at the present time the most general height is 11 feet 6 inches to 13 feet 9 inches, furnaces with a height of 17 feet 6 inches being only occasionally used there for charges rich in silica, one at the Globe Smelting Works at Denver having this dimension.

The depth from the tuyere level to the lowest point of the hearth (crucible or well) varies according to the nature and size of the

furnace from 20 inches to 3 feet. It must not be more than 3 feet, otherwise the lead in the hearth might become too cold. In the Freiberg Pilz furnace it measures 2 feet; at Friedrichshütte, near Tarnowitz, 2 feet 1½ inches; in the Raschette furnace of Altenau 2 feet 8 inches to the hearthstone; and in American furnaces 3 feet to 3 feet 3½ inches.

In horizontal section, furnaces of the present day are circular or rectangular.

Circular furnaces must not exceed a certain diameter, otherwise the air at the pressure employed cannot force its way to the axis of the furnace, and a cold central core is the result. If the air pressure be increased, lead is volatilised, iron begins to be reduced, and the melting zone extends upwards in the furnace.

The pressure of the blast in circular furnaces lies between ¾ of an inch and 1½ inches of mercury, varying with the size of the furnace and the fusibility of the charge. In the case of large furnaces of rectangular section, it is higher—from 2 to 2½ inches of mercury.

The diameter of the furnace at the tuyere level should not exceed 5 feet. The Freiberg Pilz furnace (Muldener Works) has a diameter of 5 feet, and a blast pressure of 1⅜ inches of mercury; a round furnace at Przibram 1½ inches pressure, and 4 feet 7 inches diameter; the new furnace at Friedrichshütte ⅞ inch pressure, 4 feet 1 inch diameter; the Schemnitz furnace 1 inch pressure, 4 feet diameter.

In the United States the diameter does not usually exceed 42 inches, and the blast pressure 1 to 2 inches of mercury. One exception, a furnace designed by Probert of 6 feet 10 inches diameter, with water cooled tuyeres projecting 2 feet into the furnace, does not, however, seem to have come into actual use.[1]

Furnaces of circular horizontal section can only treat a certain quantity of ore, as they must not exceed a certain definite area at the tuyere level. Furnaces of rectangular section, however, permit of their area at the tuyere level being greatly increased as compared with a circular furnace, as the two longer sides may be extended without altering the dimensions of the shorter side, and without any consequent increase in diameter with its attendant disadvantages. Where a large amount of ore has to be quickly worked, it is therefore better to employ rectangular than circular furnaces.

Such furnaces have been used for some time in the United States, principally in smelting lead ore, the circular furnaces being only used for working up the bye products. The short sides of the rectangle are from 30 to 42 inches in length, the longer sides were at first 6 feet,

[1] Eissler, *Metallurgy of Argentiferous Lead*, 1891.

but were subsequently increased to 10 feet, which is the usual size of furnace now in use. The extreme length of 11 feet 8 inches is employed in a furnace of the Globe Smelting Works at Denver, designed by Iles. All the American furnaces are furnished with water-jackets, and a furnace 2 feet 9 inches by 8 feet 3 inches at the tuyere level, with five tuyeres $3\frac{1}{4}$ inches diameter on each side working at $1\frac{3}{16}$ inches pressure, can treat 40 tons of ore in the 24 hours. The Altenau Raschette furnace is 3 feet $2\frac{1}{2}$ inches by 6 feet 6 inches at the tuyere level.

In vertical section the furnace expands from the tuyere level to the throat. This expansion may either be gradual, or else the furnace widens sharply from the tuyeres upwards to a certain point (the boshes) and then widens more gradually to the throat. Sometimes the furnace walls go vertically upwards above the boshes, or possess even a slight inward slope, in the latter case usually when zinciferous ores are being worked. When the ores are very rich in zinc, as in the Lower Harz, it is usual to belly out the furnace above the tuyere level, in order to prevent its being quickly contracted by zinciferous deposits.

Circular furnaces usually widen uniformly from the tuyere level to the throat, but rectangular furnaces are generally provided with well-marked boshes. These furnaces have proved to be so efficient in the States that it seems probable that lead ore smelting will soon be entirely effected in such rectangular furnaces with boshes.

The following are dimensions of various furnaces in use:

As examples of a furnace without boshes, the circular Pilz furnace at the Muldener Works, Freiberg, is 17 feet 7 inches high from the tuyere level to the throat, 5 feet in diameter at the former, and 6 feet 7 inches at the latter; the new Schemnitz furnace is 11 feet 6 inches high, 4 feet diameter at the tuyeres, and 5 feet at the throat; one of the Friedrichshütte furnaces at Tarnowitz has a height of 12 feet 4 inches, is 4 feet in diameter at the tuyeres, and 5 feet 8 inches at the throat: the other is 14 feet 9 inches high, 4 feet in diameter at the tuyere level, and 6 feet 7 inches in diameter at the throat.

Among the rectangular furnaces without boshes, the Altenau Raschette furnace is $16\frac{1}{2}$ feet high from the tuyeres to the throat, 3 feet $2\frac{1}{2}$ inches by 6 feet 7 inches at the tuyeres, and 4 feet 5 inches by 7 feet at the throat.

Of American furnaces rectangular in plan, and furnished with boshes, the furnace of the Omaha and Grant Smelting Works at Denver may be taken as an instance. It measures 3 feet by 6 feet

8 inches at the lower end of the boshes, and 4 feet by 7 feet 10 inches at the upper end of the boshes, which are 3 feet 6 inches high. It then widens upwards to the throat, which is 12 feet 3 inches high, and there it measures 4 feet 10 inches by 8 feet 6 inches.

In recent furnaces the tuyeres are arranged symmetrically round the furnace. Tuyeres at the back of the furnace only are rare now, though they were formerly used in that way when smelting with a *nose*, the ore and fuel being charged in vertical columns.

With the smaller furnaces previously used, only 1 to 3 tuyeres were employed, whilst with the large circular and rectangular furnaces of the present day, 8 and 12, and even as many as 14 tuyeres are used. At Freiberg the later Pilz furnaces have 12 tuyeres, the older ones only eight; the Raschette and American furnaces have 12 to 14 tuyeres; furnaces with less than three tuyeres are now never used Rectangular furnaces were at first provided with a tuyere in each of the shorter sides, but this arrangement has in most cases been done away with on account of its inconvenience, and practically the same result has been attained by putting a tuyere in the longer sides close to the ends of the furnace.

Construction of the Furnace

The type of furnace that should be used as a rule is the crucible furnace. Furnaces provided with a fixed forehearth (*sumpföfen*) are occasionally used in the smelting of highly zinciferous ores, where the hearth has often to be freed from various accretions and bears. Furnaces with independent forehearths in which the lead produced ran out continuously instead of accumulating inside (*spurōfen*), are now no longer used, as the separation of the lead from the molten mass in the forehearth was very incomplete.

The crucible furnace has the advantage of retaining its heat better than any other variety, so that the molten mass at the bottom of the furnace is maintained in a perfectly fluid condition, thereby ensuring a complete separation of the various ingredients composing it. The slag in particular can be very perfectly separated from the lead, it being either allowed to flow continuously out of a slag notch and down the slag spout into iron pots, or else it is tapped off at intervals of from 5 to 10 minutes through a tap hole made up with clay or brasque and provided with a short spout. By periodically tapping the slag, which is the method chiefly practised in the United States, the heat is more perfectly retained in the furnace, and the slag is rendered so completely fluid that it can traverse a series of pots and be transported considerable distances without the mass solidifying.

Furnaces of medium size have usually only one slag notch, whilst furnaces of large capacity producing large amounts of slag have two, which are tapped alternately. Rectangular furnaces are provided with two slag notches, one in each short side, in order to prevent the molten mass from cooling, as it would do on the farther side if there were only one tap hole. The details of the slag notches will be shown subsequently under the head of American furnaces.

The running off of the lead from both crucible and well furnaces takes place either periodically or goes on continually, the matte and speiss being only withdrawn at intervals. Periodical tappings are made as soon as the crucible or well is full of molten material; the blast is shut off, and the molten lead, matte and speiss are allowed to run through a tap hole in the lower portion of the crucible into a tapping hearth or vessel placed to receive it. The sudden withdrawal of this molten mass leaves a cavity at the bottom of the furnace into which the unfused charge can fall, causing a risk of the formation of *bears* or furnace accretions on the hearth. This risk is lessened by allowing some lead to remain in the hearth, so that the portions of the charge fall only on to its surface, and floating there cannot come into contact with the hearth bottom. A further objection to periodical tappings is that the stoppage of the blast and the emptying of the crucible both delay the process and cool the furnace.

The continual withdrawal of the lead from the crucible or well is effected by means of a *syphon*, the fluid mass inside the crucible forming one leg, the other being a sloping hole extending down to it, with its open mouth outside the furnace. The molten lead thus stands at the same level outside the furnace as it does inside, or on account of the pressure of the blast or of the superincumbent mass of the charge on the lead inside, it will always be found to be slightly higher on the outside. By widening the mouth of the tube leading outside the furnace or making it bowl-shaped, the molten lead can be ladled out and then cast into moulds, or it can be tapped from this or allowed to flow over into another forehearth.

This contrivance for continuously drawing off the lead known as the *syphon tap* or *automatic tap* was introduced by Arents, a Clausthal smelter, and first employed by him in Nevada; it has since been introduced into all the American smelting works, and a certain number of the European ones. The arrangement now used in America is shown in Fig. 226; b is the crucible and d the channel communicating with it, at the upper end of d is a bowl c from which the spout a' conveys the molten lead.

In the modern American furnace, the whole arrangement forms

part of the furnace base, the crucible, communicating pipe and its well at the top being all enclosed by the iron plates and buck staves that form the outer wall of the furnace base, whilst in the older furnaces the mouth of the pipe lay outside the wall of the hearth. This latter arrangement is employed in European furnaces as shown in Fig. 227, which represents the Arents tap applied to a Schemnitz round furnace; *a* is the inner portion of the tube communicating with the crucible, *h* is the expansion at the mouth of this tube in which

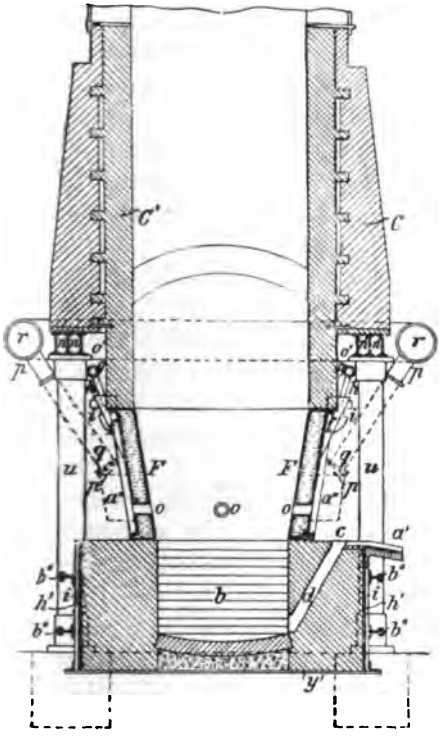


FIG. 226.

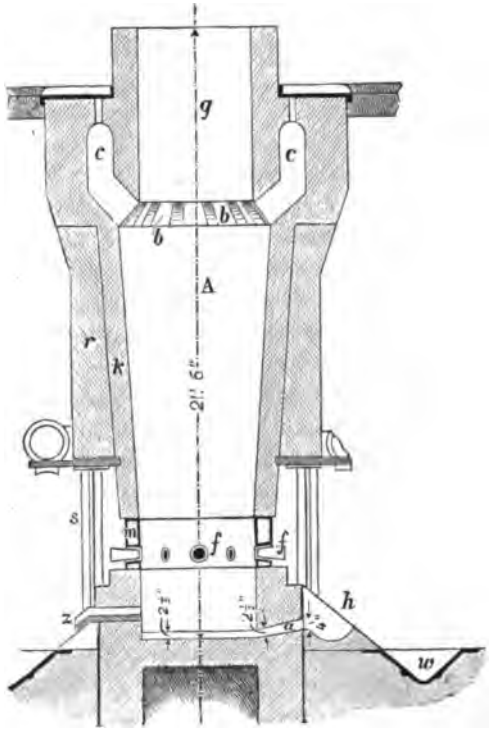


FIG. 227.

the lead collects and flows over into the cast-iron forehearth *w*. In the first instance, the tubes were constructed of cast-iron, ending in a cast-iron basin lined with clay. Cast-iron pipes are now no longer employed, the channel being made of the same material as that of which the hearth itself is composed. In the United States, where the hearth is generally made of fire-brick, the pipe is constructed of a similar material and is square in section and from 3 to 4 square inches in area. The hearth walls are seldom less than 22 inches

thick. In the case of brasque hearths the connecting pipe is cut out of the substance of the hearth itself. When the furnace has to be blown out, the lead in the hearth can be tapped off by a special tap-hole.

The syphon tap can also be used when matte and speiss are being produced. When the slag is tapped off at intervals, as is generally the case in American practice, the matte and speiss go with it into the slag pots, and there arrange themselves according to their specific gravities. In those cases where a periodical tapping of the slag is not made, the matte can be run off through a special tap hole placed below the slag outlet.

Arents's tap cannot be employed if the charge is rich in copper, as a difficultly fusible copper-lead alloy is formed, which is liable to solidify on the hearth bottom, and cause a stoppage of the communicating channel. To a certain extent this can be prevented by leaving sufficient sulphur into the charge to form copper sulphide which then goes into the matte, but, if the copper content of the charge amounts to more than 10 or 12 per cent., the formation of the copper-lead alloy cannot be prevented.

The advantages attending the employment of the automatic tap are, that by the continuous withdrawal of the lead the unhealthy operation of tapping is dispensed with, that, as a certain amount of molten lead is always left in the hearth, the risk of the formation of bears and accretions on the furnace hearth is lessened, and the emptying of the hearth and its exposure to the cold blast are avoided. This method of running off the lead is consequently to be preferred, except in those cases where there is a risk of the passage becoming blocked.

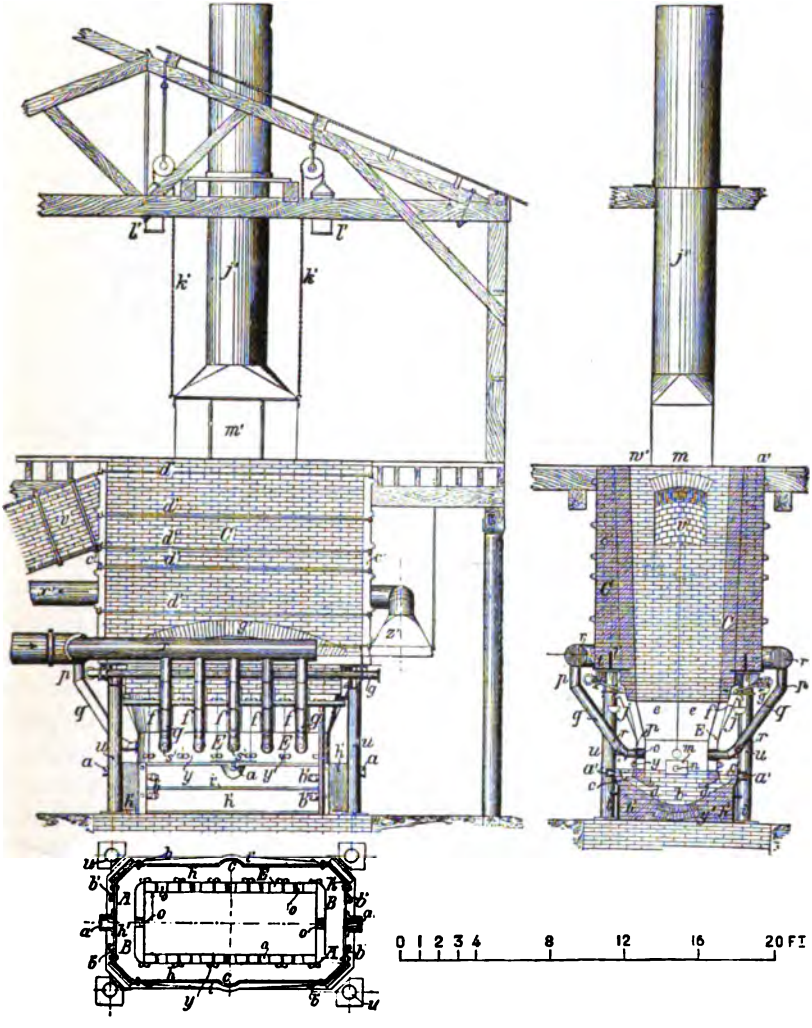
In the recent types of furnace those portions of the furnace walls surrounding the zone of fusion are water-jacketed, being made hollow and filled with water. This water-jacket may be constructed either of cast-iron, cast-steel or wrought-iron, the latter, in the form of boiler-plate, being usually used on account of its durability; jackets of cast-steel have answered well at the Hanau Works near Salt Lake City, Utah.[1]

Water-jackets are used with both circular and rectangular furnaces; in the former case they are built up of hollow segments of a circle, and in the latter of rectangular boxes connected one to the other by bolts, in each case being provided with holes for the passage of the tuyeres through them.

The water-jackets of circular furnaces are usually placed vertically,

[1] *Trans. A.I.M.E.* xvii. p. 131.

those of the rectangular furnaces sloping outwards to the boshes, this form being the one mainly adopted in the recent forms of rectangular furnace employed in the States. Where cast-iron is employed

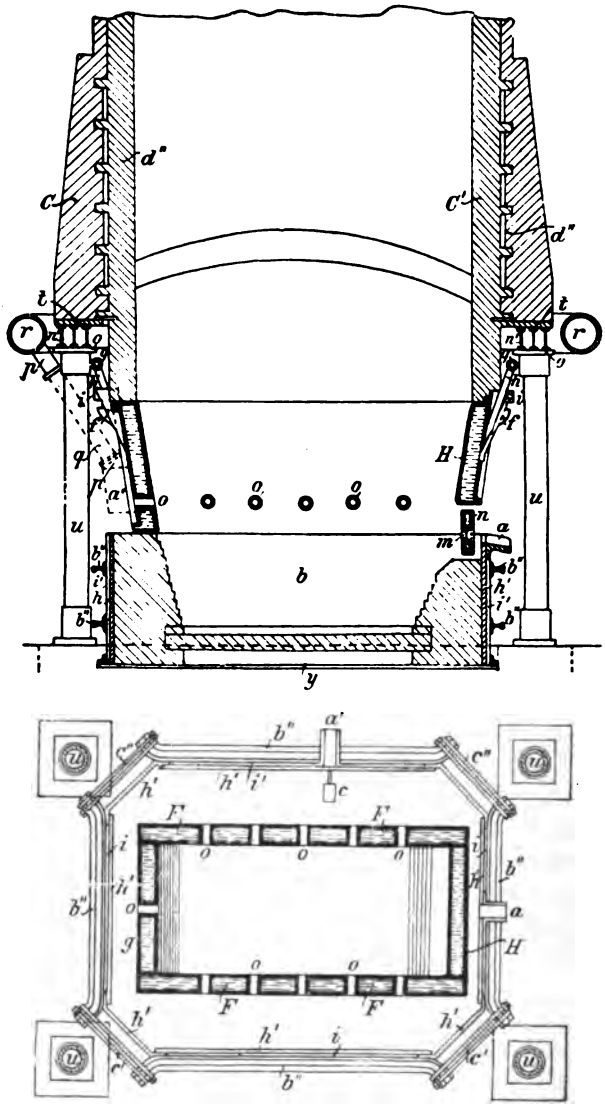


FIGS. 228—230.

the jacket is bent to correspond with the angle of the boshes, whilst with wrought-iron jackets the slope is uniform.

The construction of a furnace with cast-iron water-jackets is shown in Figs. 228 to 230, and that of a furnace with wrought-iron jackets

in Figs. 231 to 233.[1] In the first figures E is the water-jacket, constructed of a series of cast-iron boxes. The width in the clear



FIGS. 231 AND 232.

is 6 inches, and the thickness of the iron ½ an inch. The separate sections are joined to each other by bolts passing through lugs

[1] Hofmann, *Metallurgy of Lead*.

y and secured by nuts. The cold water flows through a common pipe g into the separate pipes h, and from these into the jackets by a feeder f, fastened on to the outer wall.

The cold water sinks down and the warmer, lighter water overflows into a trough j running round the furnace. The air is blown in through the holes o. The mud which accumulates in the interior of the jackets is periodically cleaned out through openings in their lower parts, not shown in the drawing, and which are ordinarily closed by iron doors. The slag notch shown at n is a hole made through the jacket and is thus kept cool by the surrounding water. The entire jacket rests upon the top of the hearth walls and its height averages about 3 feet. The centres of the holes for the tuyeres are 10 inches from the bottom of the jacket, and 10 inches above this the jacket begins to slope outwards.

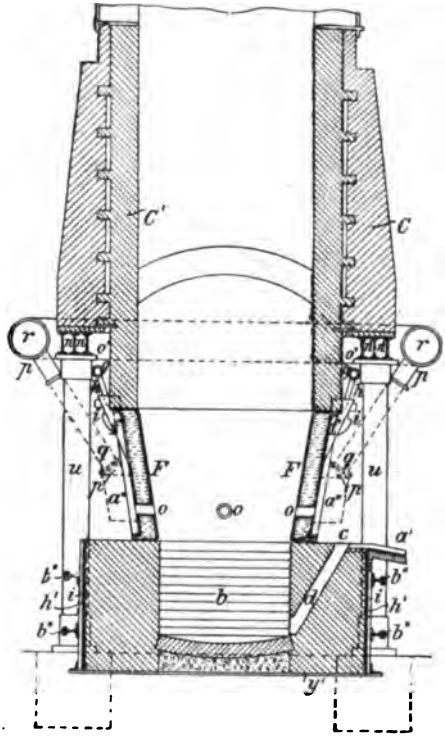


FIG. 233.

Figs. 231 to 233 show the arrangement of a furnace with wrought-iron water-jacket. F is the jacket, o, o are the holes for the tuyeres, f, f are the feeders screwed on to each separate compartment, the latter discharging their warm water through the spouts i, i. There are four separate compartments forming the jacket, one on each side of the furnace. The slag notch m is conical, widening from $2\frac{1}{2}$ to 5 inches, and is provided with a water-jacket n. For an American furnace measuring 3 feet by 3 feet 6 inches at the tuyere level, and producing a slag rich in lime, 11 gallons of water per minute are required.

Circular furnaces are also fitted with both cast- and wrought-iron jackets, wrought-iron being principally used in the States; as many as twelve segments may be employed. The cold water enters at the lower part of each segment, the hot water flowing away by

another tube from the top. The water-jacket of the earlier Pilz furnaces at Freiberg was made up of eight segments, the later ones having twelve made of iron plate. They are 19½ inches high and 8 inches wide inside. Figs. 234 to 236 represent the Freiberg furnace with eight segments. Water cooling should always be employed whenever a sufficient supply of clean water can be procured.

The pressure of the blast varies according to the nature of the charge and the size of the furnace, from $\frac{9}{16}$ to 2½ inches of mercury.

The tuyere nozzles vary from 2 to 3½ inches in diameter, the average size in use in America being 3 inches diameter, a tuyere of this size sufficing according to Hahn[1] for an area of 2 square feet at the tuyere level.

The blast is generally produced by a blower, as these are inexpensive and furnish air at the requisite pressure. In Europe Root's blowers are exclusively employed, Baker's blower being chiefly used in America and Australia. Latterly, however, Root's blowers have come into use in the States.

The blast is introduced into the furnace through tuyeres or, in some of the water jacketed furnaces, simply through holes in the jacket, a wind chest running round the jacket connected with the main supply pipe, and the blast passing through the holes without the intervention of tuyeres. This arrangement, shown in Figs. 231 and 232, possesses the advantage of preventing any loss of blast. The blast chamber is furnished on the far side with two openings which can be closed at will; through the upper one tools can be introduced into the tuyeres, whilst the blast and furnace gases escape through the lower one.

Hot blast is not advantageous in lead smelting as it is in the case of iron smelting, a high temperature not being necessary. The saving in fuel which would be effected by its employment would be more than counterbalanced by the increased loss of lead through volatilisation owing to the high temperature, and there would be the danger of producing iron *bears* owing to the reduction of metallic iron.

Examples of furnaces which have been and are actually in use will be found in the following pages.

OLDER FORMS OF FURNACE

The earlier furnaces in which the charge was introduced in vertical columns are now generally replaced by large furnaces

[1] *Mineral Resources of the United States*, 1882, p. 336.

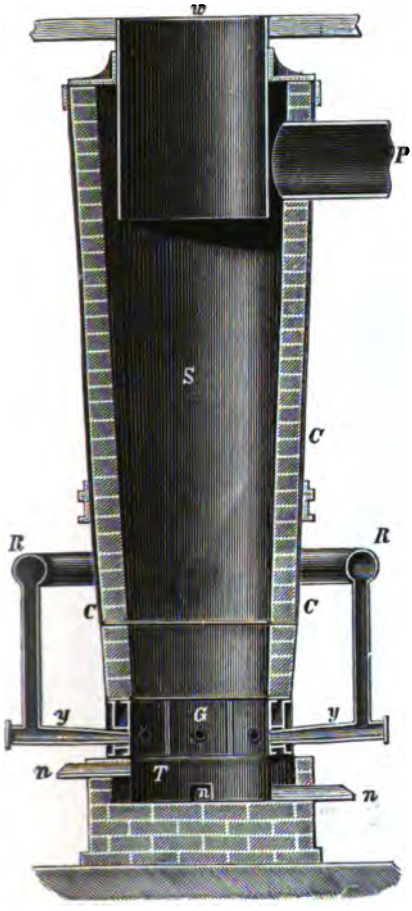


FIG. 234.



FIG. 235.

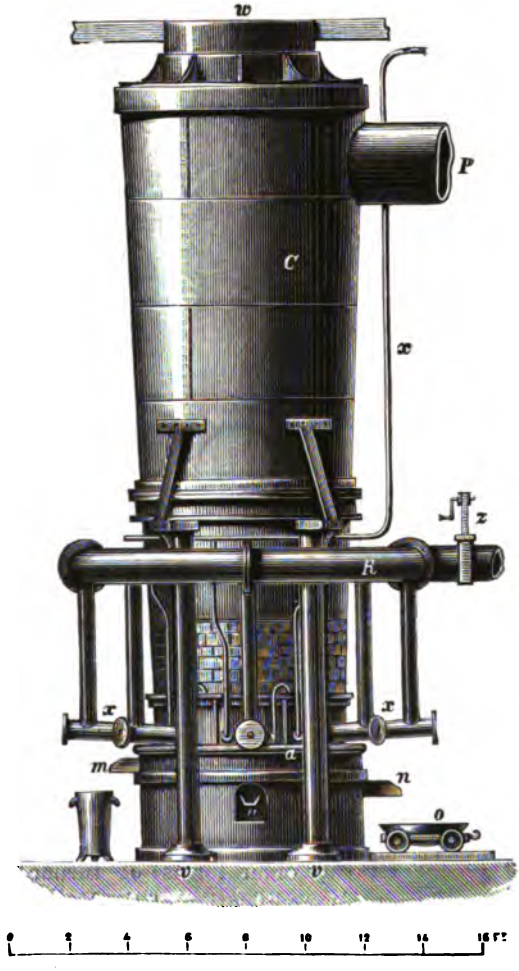


FIG. 236.

which are charged in horizontal layers, and they consequently are only of historical interest and will be but briefly noticed.

The *krummöfen* were low furnaces charged from the floor level, square or trapezoidal in horizontal section and provided with one or two tuyeres at the back, the charge being introduced in vertical layers. The process was so conducted that the furnace top was bright and the fuel consumption, loss of metal, and expenditure in wages were all high.

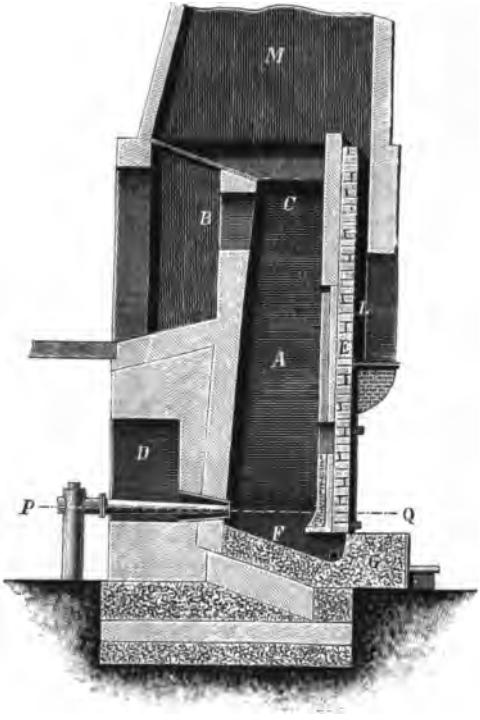


FIG. 237.

Of the older forms of furnace the old Lower Harz furnace, Wellner's modification of the Vogel furnace, and the Stolberg furnace will be briefly described.

The older furnace in use in the Lower Harz, shown in Figs. 237 and 238, was a furnace of trapezoidal horizontal section, with two tuyeres, and with continuous forehearth or well. The shaft was gradually narrowed by the slope given to the back wall. *A* is the furnace shaft, *c* the retaining walls, *m* a hood for carrying off the fumes, *h* the tapping pot, *k* the slag channel, *g* the forehearth, *f* the well, *d* the tuyere arch, and *b* the charging door. At the lower end of

the inner front wall is the so-called "zinc stool" (*zinkstuhl*). This consists of a horizontal plate of slate placed at right angles to the front wall, and fastened to this is a vertical plate of slate. Charcoal is put on the horizontal plate and reduced zinc and some lead collect there, the reduced metals flowing through a spout in the front wall to a small well placed outside the furnace. When coke replaced charcoal as fuel, zinc no longer condensed in the *zinkstuhl* on

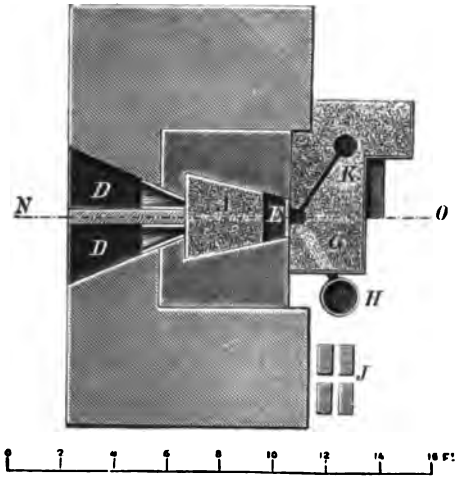


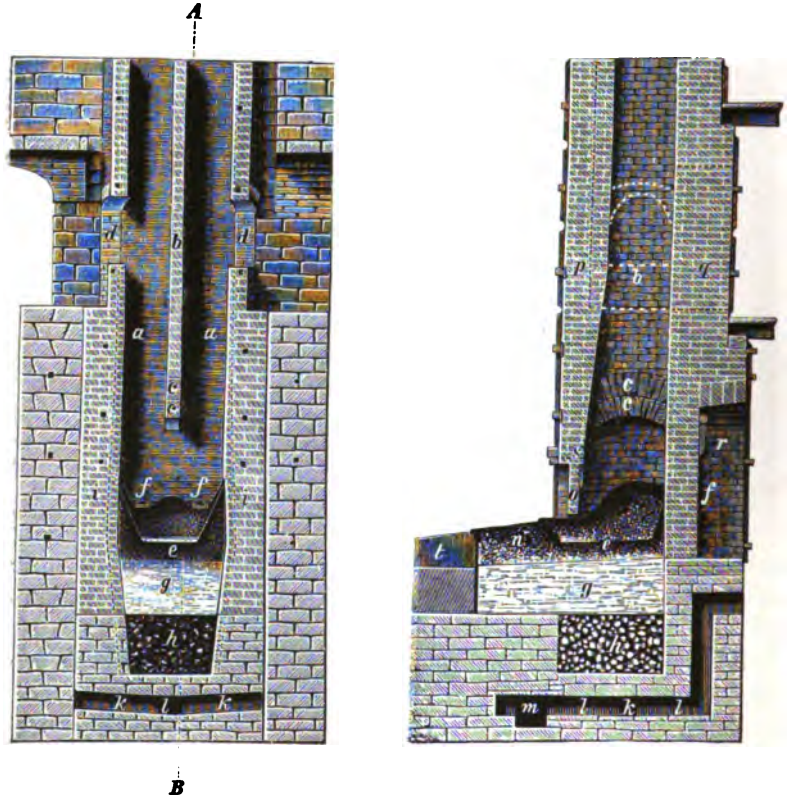
FIG. 238.

account of the higher temperature and the increased amount of carbon dioxide produced, this gas exerting an oxidising action on the zinc.

The ore and fuel were charged in vertical columns, the ore at the back, the fuel at the front. The blast pressure was 1 inch of mercury. The process was carried on with a hot top in order to volatilise the zinc in the ore. The furnaces treated about $7\frac{1}{4}$ tons of ore or 12 tons of total charge per day, but the campaign only lasted 10 or 12 days, as by that time the furnace had become so constricted, owing to zinciferous deposits, that regular working was impossible. These furnaces are now replaced by the circular furnaces described on page 369.

Wellner's modification of Vogel's furnace, formerly in use at Freiberg, is represented in Figs. 239 and 240. Wellner modified the furnace, by introducing a partition wall *b*, in order to secure a regular descent of the vertical columns of fuel and ore; *k*, *l* and *m* are channels to carry away any moisture from the foundations, *h* is

a slag foundation, and resting on it are layers of loam *g* and of brasque *e*, the furnace well being made out of the latter; *n* is the slag channel, *i*, *i* are the vertical furnace sides, *p* is the front wall sloping outwards from the top, *o* is the breast wall, *r* the tuyere arch, *d*, *d* the charging openings, and *f*, *f* the tuyeres. This furnace is now replaced by the Pilz furnace described on pages 363 and 368.



FIGS. 239, 240.

The Stolberg furnace, also formerly in use at Freiberg, is shown in Figs. 241 to 243. This is a furnace of trapezoidal section, diminishing towards the base and furnished with a sump or well; *k* is the lining of the shaft, *r* the retaining wall, *s* the sump, and *h* the forehearth. *m*, *m* are two tapping pots made of brasque, *n*, *n* are the tuyeres in the back wall, *z* is the charging opening, and *w*, *w* are drainage channels to keep the foundations dry. These furnaces have also been replaced by Pilz furnaces.

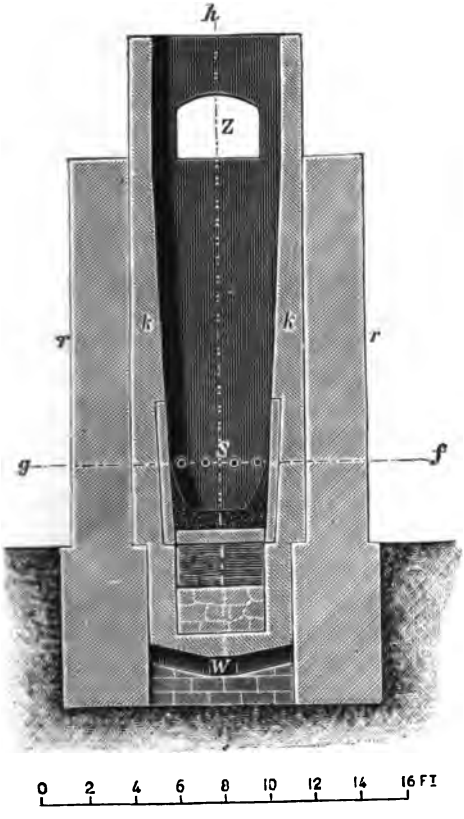


FIG 241.

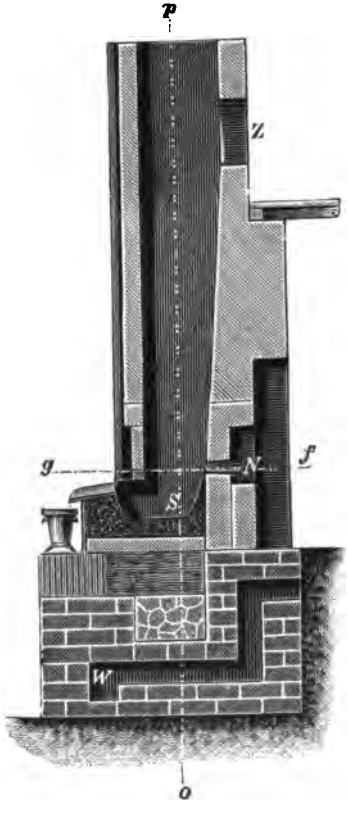


FIG. 243.

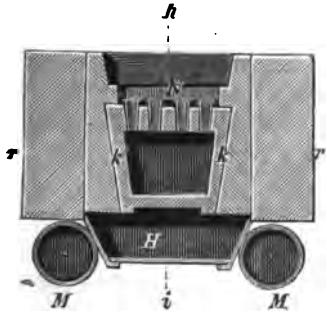


FIG. 242.

RECENT FURNACES

Recent furnaces are either circular or rectangular in section. If a large output is required, rectangular furnaces have the advantage over circular ones.

The Freiberg or Pilz furnace, the Przibram furnace, and the recent furnaces in use in the Lower Harz will be taken as examples of circular furnaces, and the Raschette and modern American furnace of those of rectangular section.

The Freiberg or Pilz furnace with eight tuyeres has already been figured (Figs. 234 to 236). In these illustrations *s* is the shaft, *c* the inner lining surrounded by boiler plate, *v*, *v* are cast iron columns carrying the iron jacket and most of the brickwork. *T* is the crucible with walls of fire-brick, *n*, *n* are spouts for running off the matte, speiss, and lead into vessels, *o*, *o*, placed to receive them, *m*, *m* are slag spouts through which the slag flows alternately. The water jacket *g* is composed of 8 hollow iron segmental boxes bolted together so as to form a circle, each section being 8 inches deep and 20 inches high. The nozzles *y*, *y*, are short tubes passing through holes in each water jacket, *w* is a cylinder of iron plate hanging in the throat of the furnace, the furnace gases passing round it and away through the flue *p*. The entire shaft is 26 feet high, 6 feet 6 inches in diameter at the throat, and 5 feet diameter at the tuyere level. The newer furnaces possess 12 tuyeres instead of 8, their height from the hearth to the top varies from 17 to 27 feet 8 inches, and the diameter at the tuyere level is 5 feet, and at the throat 6 feet 7 inches. In 24 hours 30 to 35 tons of ore and the same amount of slag are put through with a blast pressure of nearly 1 inch of mercury. One ton of coke is required for every 15 tons of charge, the charge containing on an average 20 to 30 per cent. of lead and 10 per cent. of zinc.

The majority of lead smelting furnaces on the Continent are constructed on the type of these furnaces, first designed by the late Bergrath Pilz of Freiberg and called after him.

The Przibram (Bohemia) furnace illustrated in Figs. 244 and 245 has an inner lining enclosed in a retaining wall, 8 tuyeres, and 3 sets of hollow cast iron cooling rings placed one above the other; the lead is continuously withdrawn from the furnace by means of Arents's automatic tap.; *f* is the slag spout, *d*, *d* are the supporting columns, and *b*, *b* supports for blast pipes, which are not carried like the others by the supporting columns; a thick iron plate forms a foundation for the interior of the furnace and the hearth is constructed out of brasque. In such a furnace, 29 feet high, 4 feet 7 inches in diameter at the tuyere level, and with a blast pressure of 1½ inches of mercury,

8 tuyeres of 2½ inches diameter are used, 31 tons of a charge containing 22 tons of ore can be smelted in 24 hours, 16·39 tons of coke and 155 bushels of charcoal being consumed.

The modern Lower Harz furnace for smelting highly zinciferous

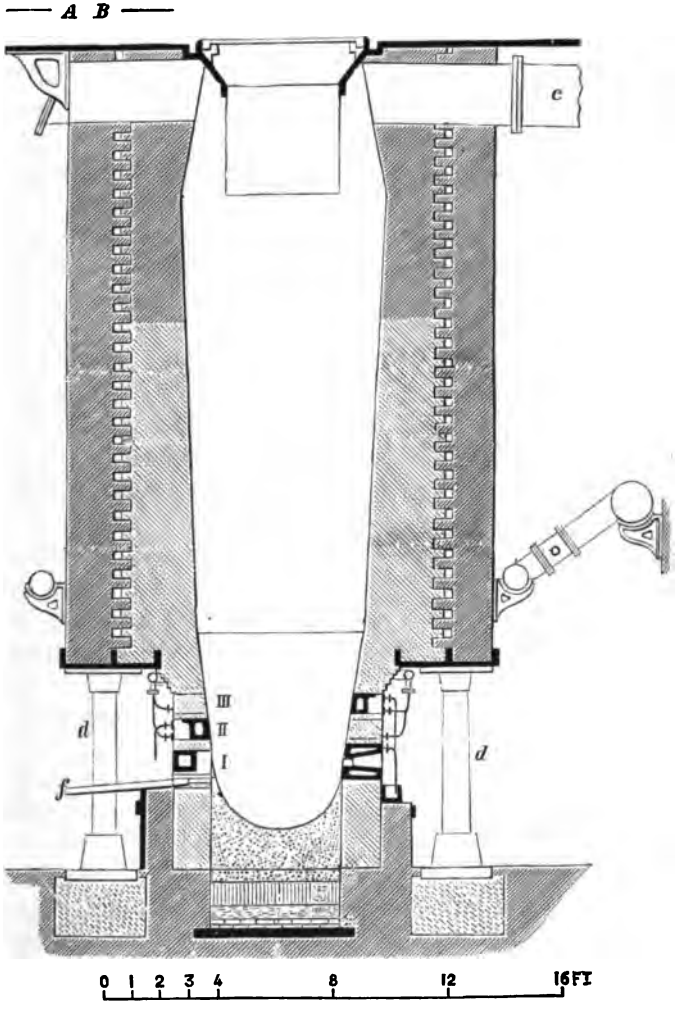


FIG. 244.

ores containing heavy spar is shown in Figs. 246 to 251. It is provided with a fixed forehearth or well hollowed out of brasque, this being used on account of the large amount of zinc present, and has 5 tuyeres, the tuyere level being 14 inches above the hearth. The total height of

the furnace is 19 feet 6 inches, and 18 feet 4 inches from the tuyere level to the throat. Above the tuyeres the furnace widens so as to allow for the contraction inevitable owing to accretions caused by the zinc; the diameter of the furnace is 20 inches at the base, 39 inches at the tuyere level, widening to 49 inches at a distance of 3 feet above the tuyeres, and narrowing again to 39 inches at the throat. The furnace is made narrower at the throat in order to increase the velocity of the gases there and so carry off the zinc vapour quickly, with the object of preventing as far as possible the deposition of furnace calamine. The waste gases pass out of the furnace through a tube suspended in the centre of the throat. The blast pressure amounts to $1\frac{3}{16}$ to $1\frac{3}{8}$ inches of mercury. There are no water jackets; the tuyeres are spray cooled, inclined at an angle of 3°, and 2 inches in diameter at the nozzle. In a furnace of this kind 8 to $10\frac{1}{2}$ tons of ore are treated in 24 hours, with a coke consumption amounting to 20 per cent. of the weight of the ore.

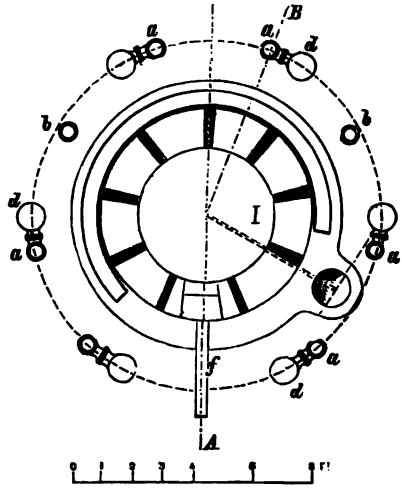


FIG. 245.

The Raschette furnace was the first of the rectangular furnaces, and is called after its inventor. It has two shorter vertical sides and two longer inclined ones, and is provided with two receivers for the molten products in front of the two shorter end walls. It is generally constructed as a well furnace with a brasque hearth and has two wells one at each shorter end of the hearth, which is consequently saddle-shaped. The tuyeres are usually placed alternately, five on each of the longer sides, either parallel to the sloping surface of the hearth or horizontally, and the furnace is often furnished with an additional tuyere in each of the shorter ends. The construction of the first Raschette furnace is shown in Figs. 252 and 253, which represent the one erected at the Altenau Works in the Upper Harz; *e*, *e* are the two wells, *v*, *v* the two working ends, *h*, *h* are passages in them for carrying the lead fume into the flues, *c*, *c* are the tuyeres, and *a* is the throat.

From the hearth to the tuyeres is 2 feet 8 inches and from there

to the throat 16 feet 6 inches. The interior of the furnace measures 3 feet 2½ inches by 6 feet 7 inches at the tuyere level, and 4 feet

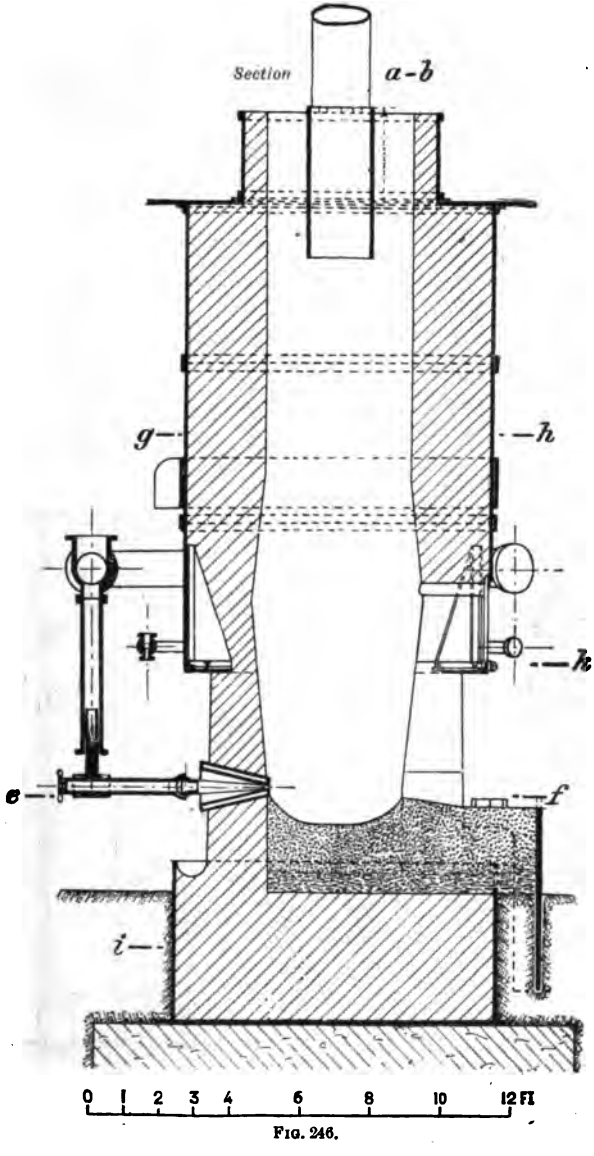


Fig. 246.

5 inches by 7 feet at the throat. The blast pressure used varies from $\frac{11}{16}$ to $\frac{3}{4}$ of an inch of mercury and the 10 tuyeres were each 2 inches in diameter. At the present time the tuyeres are placed

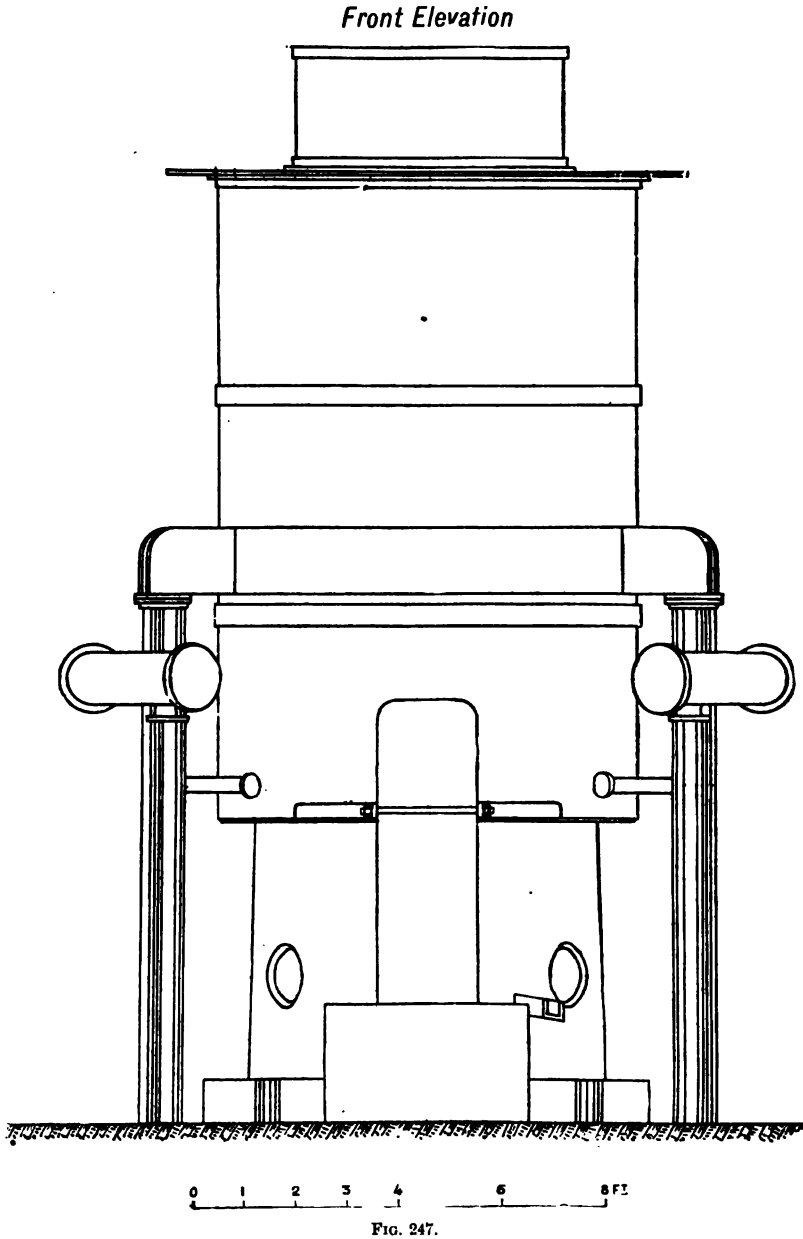


FIG. 247.

horizontally and not inclined as shown in the drawing. The furnace smelts 10 tons of roasted ore in 24 hours using 32 per cent. by weight of coke.

The construction of the American furnaces has already been illustrated by the drawings on pages 359—361.

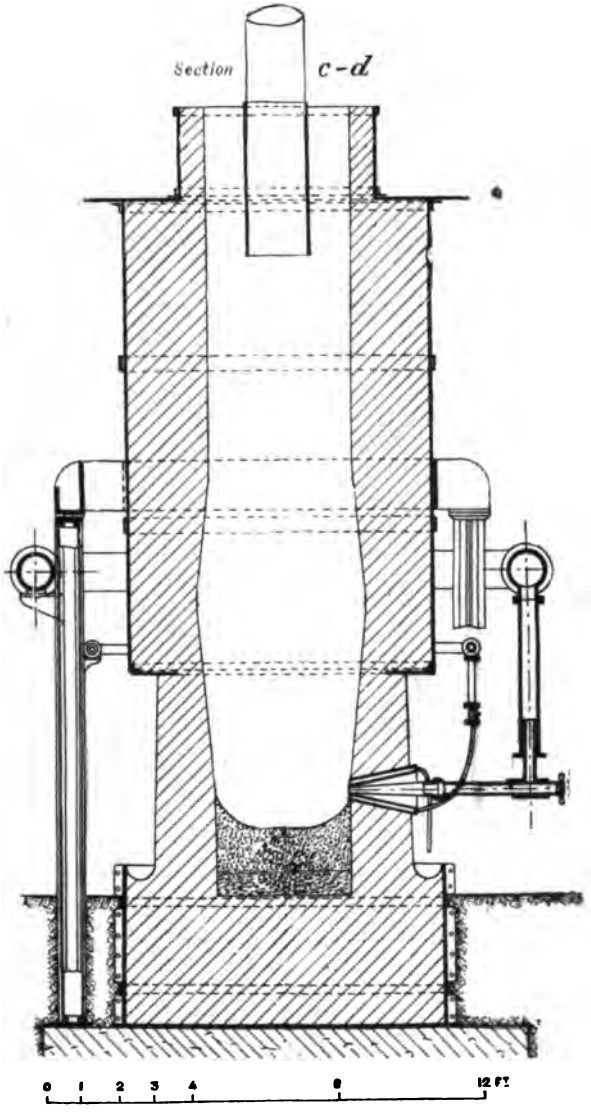


Fig. 248.

The furnace in use at the Globe Smelting Works at Denver in Colorado erected in 1891 and visited by the author in 1892 is shown

in the acompanying Figs. 254 to 256. It is provided like all modern American furnaces with a water jacket and automatic tap. Outside the inner lining it has thick retaining walls of masonry r, thickened

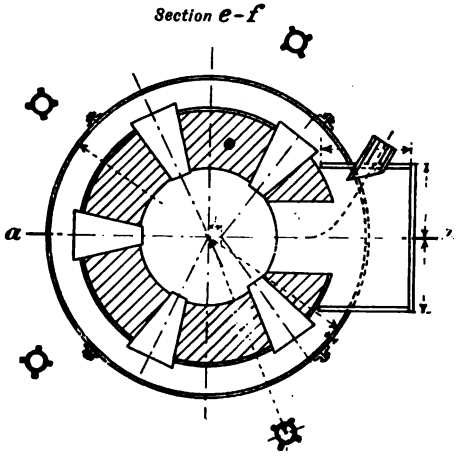


Fig. 249.

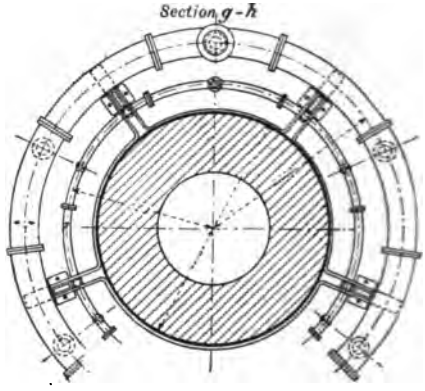


Fig. 250.

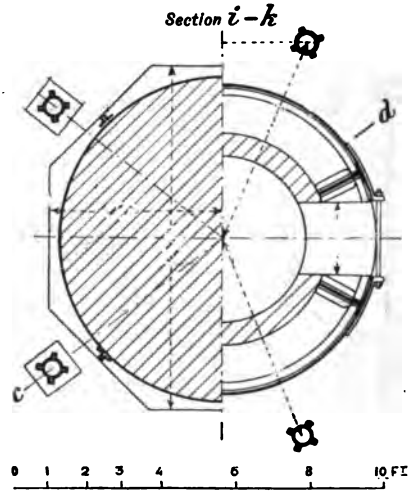
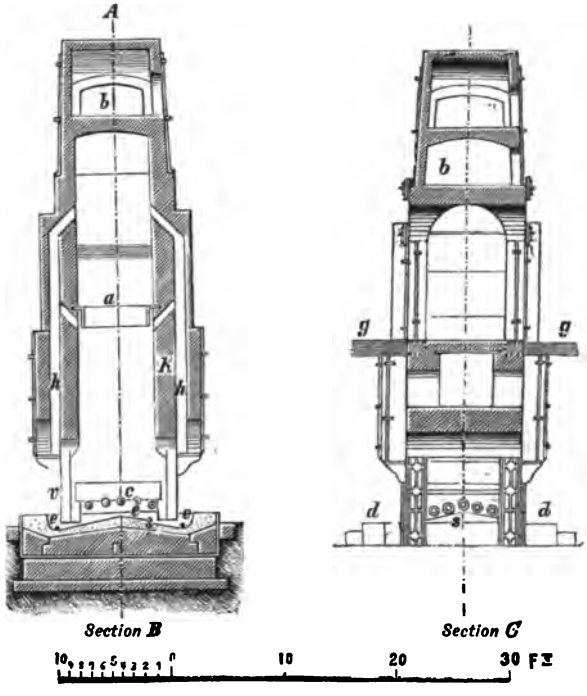


Fig. 251.

below and supported on cast iron columns. By increasing the thickness of the lower part of the retaining walls a considerable saving of fuel is effected, and at present all the American furnaces are being built in this way. w is the water jacket, h the hearth, c the Arents tap

with the enlargment *e*, *l*, *l* are the lugs by which the separate sections of the water jacket are fastened together, *f*, *f* are the holes for the tuyeres, *h* is the blast main, and *x*, *x* the tuyere pipes. The main water supply comes through the pipe *y*, being delivered to each separate compartment by pipes *z*. The slag runs off through a hole *u* in the water jacket *v*, *r'* are openings for cleaning out the jackets, *w'* and *w''* are slag spouts, *o*, *o* are the tie rods binding together the masonry of the shaft, and A, A are the cast iron plates enclosing the hearth.



FIGS. 252 AND 253.

The furnace has a height of 14 feet 8 inches from the tuyere level to the throat, the water jacket is 3 feet 5 inches, the crucible 2 feet 6½ inches high, and at the tuyere level the furnace measures 10 feet by 2 feet 6 inches. There are 12 tuyeres, 6 in each of the longer sides.

A very similar furnace, in use in Colorado, is shown in Figs. 257 to 261; this measures 8 feet 4 inches by 3 feet internally, and the other dimensions are shown in the illustrations.

One of the largest furnaces of this kind was in course of construction at the Globe Smelting Works at the time of the

author's visit to Colorado. It was 11 feet 8 inches by 3 feet 6 inches at the tuyeres, with a height of 18 feet from the tuyeres to the throat, and had 7 tuyeres in each of the longer sides.

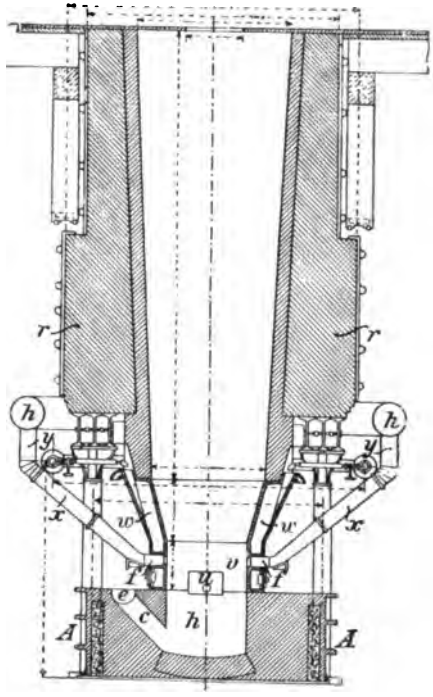


FIG. 254.

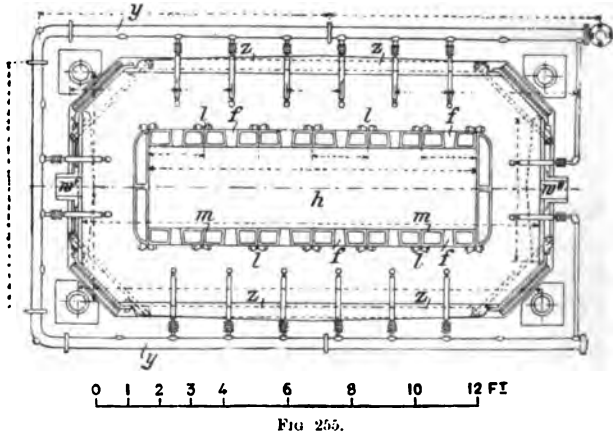


FIG. 255.

The newer furnaces at the Omaha and Grant Smelting Works at Denver, visited by the author in 1892 had a height of 13 feet

8 inches from tuyere to throat, 10 inches from the centre of the tuyeres to the bottom of the water jacket, and a hearth height of 2 feet 6 inches. At the tuyere level it measured 8 feet 4 inches by 2 feet 8½ inches. Each side of the rectangle widened out from the narrow part just above the tuyeres towards the throat to the extent of 4 inches. The hearth was built of fire-brick, like the hearths of all American furnaces, and not of brasque. There were 11 tuyeres, 5 in each longer side and one in the back wall, each of 3½ inches diameter. The water jacket was built up of 14 cast iron segments

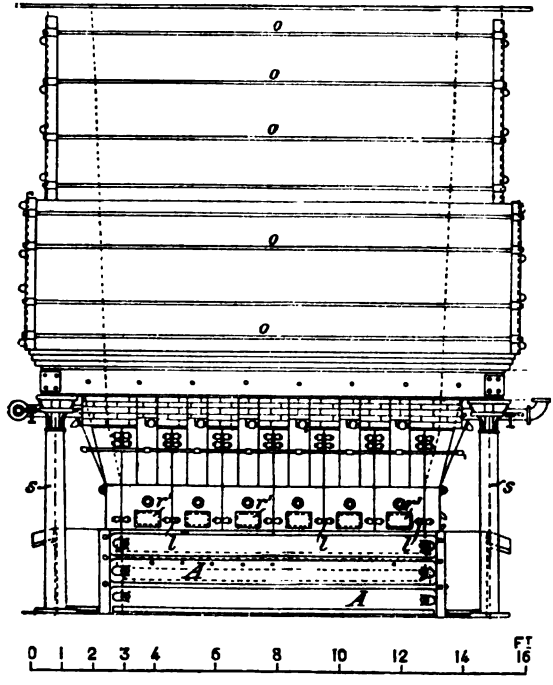


FIG. 256.

and the furnace was capable of smelting 60 tons of charge, of which 40 tons were ore, in 24 hours, the blast pressure being 1¼ inches of mercury, and the fuel used being 30 per cent. by weight of the ore in coke and 5 per cent. of charcoal.

The Smelting Process.

The manner of working varies with the character of the ores and of the fuel, as well as with the shape and size of the furnace, but is usually

conducted with the ore and fuel charged in horizontal layers and the throat dark. The amount of the charge depends again upon the nature of the ore and fuel, and the size of the furnace; as an instance, in the Pilz furnace at Freiberg which has already been described the charge amounts to 9·7 cwt. and the coke to 72 lbs. The charge, fuel, and the blast pressure for a given tuyere area are so adjusted that the resulting slag shall not contain more than 0·5 per cent. of lead. In exceptional cases as at Freiberg, slags are purposely produced by

Side elevation and Vertical Section

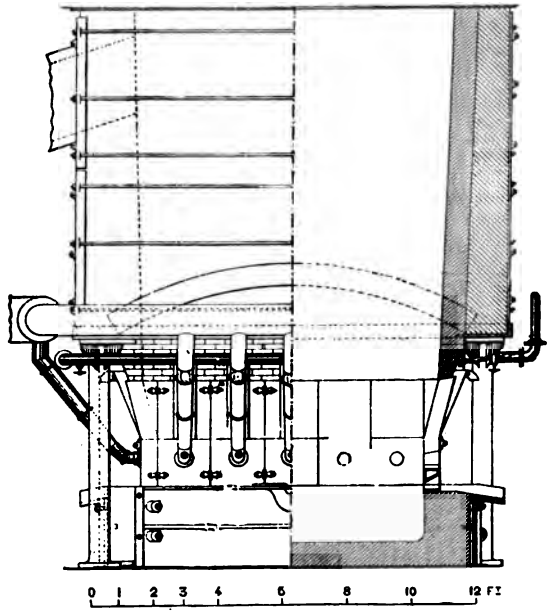


FIG. 257.

quick working which on account of their lead and silver content do not permit of their being thrown away, and in such cases they have therefore to undergo a special slag smelting, together with materials rich in iron and sulphur.

If lead matte is produced in the process as well as metallic lead, the slag generally contains some matte mechanically mixed with it. Loss from this source can be avoided by running the slag into cast iron pots in which the heavier matte has a chance of subsiding. Such slag pots are used in the United States and their general employment is to be recommended. One is illustrated in Figs. 262 to 264.

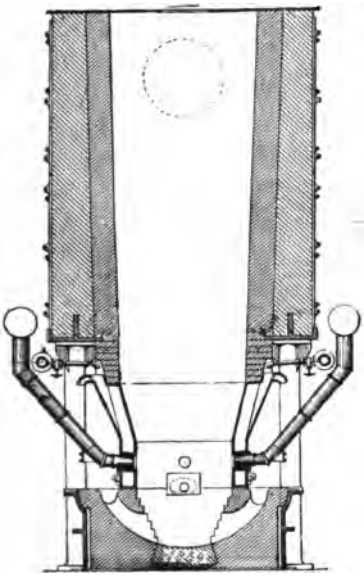


FIG. 258.

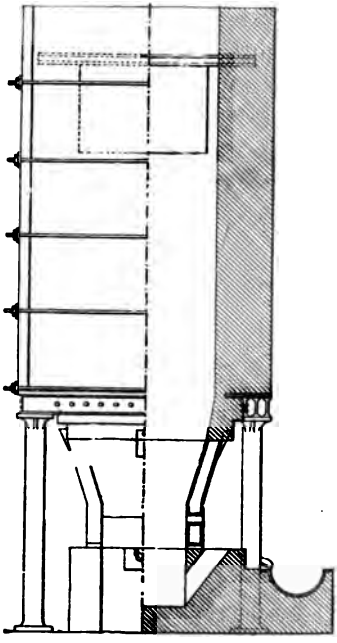


FIG. 259.

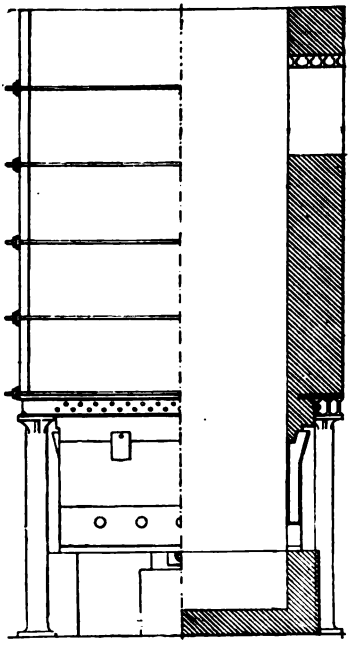


FIG. 260

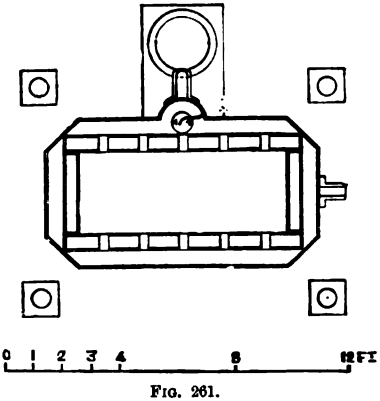
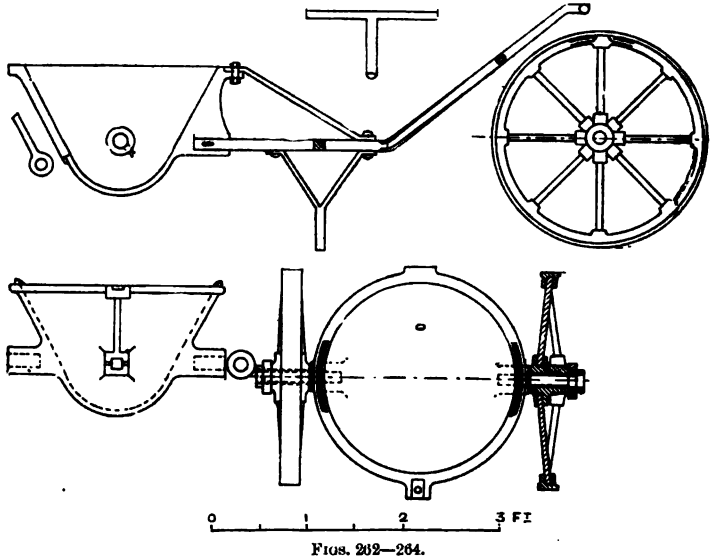


FIG. 261.

The cast iron slag pot runs on wheels and is provided with a tap hole 3½ inches from the bottom, strengthened by a flange from which a strengthening rib extends to the rim of the pot. The height of the hole from the bottom depends upon the amount of matte which accumulates in the pot.

In these slag pots the matte is allowed to settle to the bottom and thus to separate itself from the slag. The outer portions of the slag solidify, enclosing some matte, but the slag in the interior of this thin crust remains fluid and soon becomes free from entangled matte. When this is the case the still molten slag is tapped off by means of a steel rod, and the matte and solid portions of the slag remain behind. The tapped slag is thrown away, whilst the solidified shell



FIGS. 262—264.

and the matte both undergo a special slag smelting for the recovery of the lead, copper and silver contained in them. The character of the products obtained at the Omaha and Grant Smelting Works at Denver at the time of the author's visit may be cited as an example. Working in the manner just described, the waste slag contained 1¼ ozs. of silver per ton and 0·2 per cent. of lead, whilst the shell of slag remaining behind in the pots contained 4 ozs. of silver per ton. This was re-smelted, together with roasted matte and a small amount of a quartzose ore, producing lead and a matte rich in copper.

Care must also be taken in working the furnace to avoid the for-

mation of furnace bears and accretions. The separation of metallic iron, causing the production of iron bears, is caused both by the presence of an excess and of a deficiency of lime in the slag.

Deposits on the furnace walls, which are especially liable to occur during the smelting of zinciferous ores, are loosened or barred down, from above, after allowing the column of the charge to burn down low.

The temperature of the water running away from the jacket should not exceed 70°C. The volatilisation of lead is prevented as far as possible by the maintenance of a moderate temperature and by working with a dark furnace top. The lead fume is partly deposited amongst the cooler portions of the column of material in the furnace, and partly carried away with the escaping gases and condensed in suitable dust chambers, or other condensing arrangement, which should never be absent in any lead smelting works.

Products obtained by Smelting in the Blast Furnace.

The products of the roasting and reduction process are metallic lead, lead matte, slag, and in many cases speiss.

The lead, as a rule, is argentiferous, and if it does not contain too large an amount of impurity, it is submitted to the desilverising process and then is refined, or if impure it is refined before desilverising, and when necessary undergoes a second refining after that process. Lead free from silver is refined directly. The amount of silver and of other metals present in the lead varies within wide limits as the following analyses will show.

	Freiberg.	Mechernich.	Przibram.
Lead	95·088	99·513	97·359
Silver	0·47	0·021	0·423
Bismuth	0·019	...	0·007
Copper	0·225	0·133	0·11
Antimony	0·958	0·218	1·524
Iron	0·007	0·03	0·003
Zinc	0·002	0·006	0·001
Nickel	...	...	0·001
Sulphur	...	...	0·03

The lower portions of the pigs into which the lead is cast are richer in silver than the upper portions, and the portions at the centre of the top surface are the poorest in that metal.

The lead matte which is produced varies much in its character according to the amount of copper sulphide and of iron in the charge.

It seldom contains more than 25 per cent. of lead, or more than 20 per cent. of copper, usually between 5 and 12 per cent. of the latter metal. If the ores are argentiferous, the matte will be found to contain silver, and to contain more silver than corresponds to its percentage of lead if the silver were supposed to be all alloyed with the lead, so that the iron and copper sulphides in the matte must take up a part of the silver. Gold is present in the matte in much smaller amounts than in the lead.

The composition of different varieties of lead mattes from various localities will be seen from the following analyses:—

	Oker.		Freiberg.	
	I	II	I	II
Iron	30·53	30	...	40
Zinc	16·35	15	...	1·5
Copper	16·81	21	8–12	10
Lead	5·09	4	15	25
Sulphur	16·38	18	...	...
Silver	...	...	0·15 to 0·20	0·02 to 0·025

Mechernich.		Przibram.	
PbS	9·24	Pb	11·16
Cu_2S	1·95	Cu	1·50
Sb_2S_3	0·40	As	0·55
FeS	32·34	Sb	0·93
Fe_2S	51·97	Ag	0·105
NiS	0·4	Fe	41·31
SiO_2	0·31	Zn	11·55
		MnO	1·40
		SiO_2	3·06
		CaO	0·05
		S	22·23
		O	4·79

As the existence of a sub-sulphide of iron is doubtful, whenever there is not sufficient sulphur in a matte to combine with the whole of the iron, forming ferrous sulphide, the excess of iron must be regarded as being present in the metallic state. That this is the case is borne out by the fact that mattes of this character will precipitate metallic copper from copper sulphate solution.

The mattes are roasted, and if poor in copper are returned to the ore smelting, but otherwise they are smelted either alone or with additions of rich slags or argentiferous copper ores, the products being work lead and a highly cupriferous matte, the latter being subsequently worked up for its copper in a similar way to copper regulus. The details connected with the working up of cupriferous lead mattes will be found under the heading of the iron reduction process, and the processes for the extraction of the silver will be dealt with under that metal.

Treatment of the Lead Matte.

The roasting of lead matte is effected in a similar way to the roasting of copper matte or regulus, in heaps, stalls, shaft or reverberatory furnaces, and the same considerations influence the selection of the most suitable method of roasting as in the treatment of copper mattes.

At Przibram, in Bohemia, Wellner's roasting stalls are used, at Freiberg, kilns and Wellner's stalls. The stalls at Przibram hold from 65 to 140 tons of matte, and after three successive roastings the sulphur content is reduced to 8 to 10 per cent. The first firing lasts 45 to 68 days, the second 43, and the third 33 days, when 65 tons are roasted, whilst with 140 tons the times are 86, 80, and 70 days respectively. At Oker, kiln roasting is also used, the kilns being 13 feet 1½ inches high, 4 feet broad, and 7 feet 7 inches long, capable of roasting 4 to 4·5 tons of lead matte containing 19 per cent. of copper, in 24 hours. In the United States, stalls and reverberatory furnaces are both used, the latter resembling the furnaces employed in ore roasting except in being unprovided with a melting hearth. They are 40 feet long and 14 feet broad inside, the hearth being arranged in four terraces, each capable of holding 2½ tons of matte, and each terrace has two working doors on either side. Three charges of roasted ore are withdrawn every 24 hours, and between 2 and 3 tons of coal are used in that time. At the Omaha and Grant works at Denver, Colorado, where a similar furnace is used, 7½ tons of matte with 6 per cent. of copper, 8 per cent. of zinc, 4 to 5 per cent. of lead, and 60 ounces of silver per ton, are roasted in 24 hours with a consumption of 3 tons of coal, two men being required to attend to each furnace.

Rotating cylindrical roasting furnaces are only rarely used. According to Terhune,[1] a Brückner furnace at the Germania Works, Salt Lake City, Utah, 18 feet long and 7 feet in diameter, has roasted 8 tons of lead matte in 48 hours, employing the labour of one man in each eight-hour shift, consuming about 20 per cent. of coal, and reducing the sulphur in the matte to 8 per cent.

The roasted matte is either smelted together with the roasted ores in the ore furnaces or in a special furnace by itself, the furnaces resembling those previously described, though usually of smaller size and in many cases being arranged as *spurõfen*, where the molten products do not collect in the furnace but flow out as fast as they are formed. In the United States the furnaces for matte smelting are built

[1] *Trans. Am. I. M. E.* xvi. p. 19.

without crucibles, and the distance between the tuyere centres and the slag notch is only 10 inches, no automatic tap being used. At the tuyere level the furnaces measure 3 feet by 5 feet to 2 feet 9 inches by 8 feet 4 inches.

At Freiberg, the roasted matte is smelted, together with rich lead slags from ore smelting, in a Pilz furnace similar to the one already described. The charge is made up of 4 cwt. of roasted matte, 6 cwt. of slag, 9 lbs. of litharge or hearth from the cupellation furnaces, and 35 tons of coke, 60 tons of this mixture being treated every 24 hours.

At the Omaha and Grant works at Denver the roasted matte is smelted with the richer slag that forms the solid outer shell of the slag pots, in a furnace of the same size as the ore furnace but arranged as a *spurofen*. The charge is made up as follows:—

600	pounds	of slag
300	,,	,, roasted matte
30	,,	,, siliceous lead and silver ores
120	,,	,, coke
20	,,	,, charcoal

Every 24 hours 104 tons of charge are worked off with a production of 2 tons of lead, carrying 600 ounces of silver per ton, and 8 tons of matte with 20 per cent. of copper, 4 per cent. of lead, and 100 ounces of silver per ton. The matte is worked up for its copper, lead and silver, and the slag is taken off in pots with tapholes, the slag tapped from these being thrown away, whilst the shells remaining in the pots go to the ore smelting.

Speiss if produced in any quantity is roasted in order to drive off as much of the arsenic and antimony as possible, and is then smelted with metallic sulphides in shaft furnaces producing work lead, matte, and a further small amount of speiss, which is again treated in a similar way. The slags have already been described (page 346). If they contain sufficient lead and silver, they are smelted separately or together with matte or ore, whereby their silver and lead are obtained partly in the work-lead, partly in the matte produced.

The roasting and reduction method is carried on at the smelting works at Freiberg in Saxony, Langelsheim and Astfeld in the Lower Harz, Altenau in the Upper Harz, Ems, Braubach, Mechernich, Stollberg, Call, Commern, Ramsbeck, Müsen and Tarnowitz in Prussia, Przibram in Bohemia; at La Pise, Pontgibaud and Vialas in France, Pertusola near Spezzia in Italy, in the provinces of Murcia and Almeria in Spain, at Fahlun in Sweden, and in the Western States

of North America (Colorado, Utah, Nevada, Montana), as well as in Mexico and Japan. Some examples of the various methods of working will be found in the pages immediately following.

Smelting at the Sophien Works, near Langelsheim, and the Julius Works, near Goslar.

The lead ore of Rammelsberg, near Goslar, containing zinc blende, is treated at these works. After being roasted three times in heaps (page 324), the zinc sulphate formed is extracted with water, and the remaining ore is smelted in the modern form of furnace described on page 369. The average composition of the ore is as follows:—

Lead oxide	9	per cent.
Zinc oxide	25	„
Iron oxide	25	„
Sulphur (partly as SO_3)	5	„
Barium sulphate	20	„
Copper	0·75	„
Silver	0·015	„

Basic iron slags from Oker are added to the charge in order to assist in the slagging of the zinc. The charge is made up of 40 parts of ferruginous slag from Oker, 100 parts of roasted ore, and 40 parts of slag from a previous operation; the ore added is made up of 46 per cent. of lixiviated smalls and 54 per cent. of ore in lumps which have not been extracted with water.

The blast pressure is $1\frac{3}{16}$ to $1\frac{3}{8}$ inches of mercury, and there are five or six tuyeres each of 2 inches diameter; 8 to 10 tons of ore are treated every 24 hours with a consumption of 20 per cent. of coke. The work-lead obtained contains 0·1 per cent. of silver, the copper going into the slag as a matte; such rich foul slag constitutes 2 per cent. of the total slag produced and contains 5 to 7 per cent. of lead in the form of matte. It undergoes a single roasting in heaps, and is then smelted for work-lead, together with various furnace residua, basic iron slags from Oker, and slag from a previous operation.

The charge consists of 100 parts of slag and furnace residua and 20 parts of Oker slag and 30 of slag from a previous operation. In addition to the work-lead a certain amount of foul slag is produced which is again smelted in the same way, and a large amount

of poor slag which is thrown away as it only contains ½ to ¾ per cent. of lead; it has the following composition:—

Silica	16·9 per cent.
Ferrous oxide	35·05 „
Zinc oxide	19·64 „
Barium sulphate	10·24 „
Alumina	6·31 „
Lime	6·05 „

A sample of slag produced in 1887 had the following composition:—

Silica	12·87	Zinc	20·25
Alumina	3·12	Lead	0·77
Baryta	23·40	Copper	0·87
Lime	2·10	Manganese	1·48
Magnesia	0·72	Sulphur	6·40
Ferrous oxide	20·64		

The flue dust rich in zinc is collected in flues and chambers attached to the furnace. It contains considerable quantities of lead and is treated with sulphuric acid, the zinc dissolving and the lead remaining as oxide and sulphate in the residue which is added to the ore furnace charge.

Lead Smelting at Freiberg.

At the two Freiberg smelting works—the Mulden works and the works at Halsbrücke—the roasted lead ores are smelted together with silver and argentiferous copper ores, the greater part of the silver being obtained in the work-lead, whilst the copper and a portion of the silver pass into the matte.

The lead ores contain 15 to 80 per cent. of lead. Ores with 15 to 30 per cent. of lead are classed as "leady ores" (*bleiische erze*), ores with 30 to 80 per cent. of lead as galena, the average content of lead being 40 per cent., and of silver 0·35 per cent. The percentage of silver in the ores which are smelted together with the lead ores, varies from 0·005 up to several per cent. These ores are of four kinds:—

1. Copper ores with 1 to 10 per cent. of copper.

2. Zinc blende. Blendes with more than 25 per cent. of zinc are treated by themselves for that metal, the argentiferous residues

going to the lead smelting; blendes with less than 25 per cent. of zinc are roasted and smelted, together with the lead ores.

3. Arsenical pyrites and iron pyrites containing varying amounts of silver.

4. "Dry" ores (*dürrerze*). This class consists of silver ores, the gangue being either quartz or quartz and pyrites, the value of the silver in the ore being alone taken into account.

A portion of these ores is roasted in long-bedded calciners (*fortschaufelungsöfen*), and thereby freed from a part of its sulphur and arsenic, the sulphur dioxide produced being used for sulphuric acid making, and the arsenical fumes being worked up for arsenic or arsenical compounds.

The argentiferous mispickel is heated in clay retorts (*krügen*) in a gallery furnace, in order to obtain white arsenic, which volatilises and condenses in the crystalline state.

Ores consisting of a mixture of iron pyrites and arsenical pyrites, with 20 to 30 per cent. of sulphur and 10 to 15 per cent. of arsenic, are heated in clay retorts for the manufacture of arsenious sulphide (*rothglas*), the residue from this operation being then roasted and the sulphur dioxide evolved used for making sulphuric acid.

All ores containing 25 per cent. and over of sulphur, and less than 10 per cent. of arsenic, as well as the residue still rich in sulphur from the *rothglas* manufacture, are roasted in kilns when in lump form, and the ore fines in muffle or Gerstenhöfer furnaces; the sulphur dioxide produced is used in the manufacture of sulphuric acid. As the ores contain a certain amount of arsenic, arsenious oxide is given off in roasting, together with the sulphur dioxide, and this is as far as possible condensed in leaden chambers or flues, and the flue dust afterwards worked up for white arsenic (*arsenmehl* and *weissglas*).

The charge for the roasting in the reverberatory furnace is made up from the ores thus prepared, together with raw ores containing lead, copper and silver, as well as a certain amount of residues containing lead and silver, and flue dust. The mixture is so proportioned that the charge contains on an average 20 to 30 per cent. of lead, 20 per cent. of sulphur, 20 to 25 per cent. of silica, and not more than 10 per cent. of zinc, the amounts of copper and silver present depending on the way in which the charge is made up, the amount of silver as a rule varying from 0·1 to 0·15 per cent. In the roasting in the reverberatory furnace the sulphur percentage is reduced to 3 or 5 per cent., this amount being requisite to ensure the copper being collected in the matte as sulphide. The reverberatory furnace (*fortschaufel-*

ungsofen) has a hearth 44 feet 2 inches long by 10 feet 8 inches broad, the fireplace being 9 feet 10 inches by 21¼ inches (for description and illustration see pages 334–5).

The roasting is conducted so as to finally melt the charge, any zinc sulphide still present being dissolved by the double silicate of iron and lead which is formed. The ore charges in the furnace weigh 1½ tons, and one is withdrawn, the others moved up, and a fresh charge introduced, every three hours. In 24 hours 9 to 12 tons of ore are roasted with a consumption of 25 per cent. of coal, the labour of six men being required.

The roasted ores are then smelted in the blast furnaces previously described (page 368), the furnaces having a height from hearth to throat of 17 to 25 feet, a diameter of 5 feet at the tuyere level, and of 6 feet 7 inches at the throat, and working with a pressure of blast of $\frac{1}{16}$ of an inch of mercury.

The charge is made up of the roasted ores and slags from ore smelting operations, the latter being easily fusible and sufficiently ferruginous to take up the zinc contained in the ores. The iron necessary for the reduction of the sulphides contained in the charge is contained as oxide in the roasted ores. At the Muldenhütte the charge consists of equal weights of ores and slags, and 30 to 35 tons of ore are smelted in 24 hours with a coke consumption of 5·5 tons. Each furnace requires the labour of 4 men per shift, 1 smelter, 2 chargers and 1 slag wheeler.

The furnaces run from 3 to 4 years without stopping, in spite of the high percentage of zinc in the charge.

The process at the Halsbrücke works is identical with that described as being in operation at the Muldener works.

The composition of the slag which is formed has already been given (page 346). On account of its containing some 6 per cent. of lead it is not thrown away, but usually undergoes a special slag smelting, together with the matte produced during the ore smelting. The work-lead produced in the process which contains up to 1 per cent. of silver is desilverised. The lead matte produced in ore smelting contains 15 to 20 per cent. of lead, 8 to 14 per cent. of copper, and 0·14 to 0·2 per cent. of silver. It is first roasted in kilns and then in Wellner's stalls, and then generally smelted in blast furnaces, together with the slag from the ore smelting and some siliceous material, the products being work-lead and copper matte. If the lead matte was sufficiently rich in copper (10 per cent.), the matte produced contains enough of that metal to enable it to be directly treated in the reverberatory furnace, otherwise it is roasted

and again smelted in the blast furnace in order to extract the lead from it.

Speiss is sometimes produced in the ore smelting. It consists chiefly of arsenide of iron, together with nickel, cobalt, copper, lead, and some silver. This is worked up, when a sufficient amount has been accumulated, to a nickel-cobalt speiss, the further treatment of which is undertaken at the smalt works.

The slag and the matte from ore smelting are worked up by a special slag smelting, the process being carried out in a similar furnace to the one employed in ore smelting. The charge is made up of slag, roasted matte, residues containing lead, and, if necessary, some unroasted matte to furnish sulphur, the charge at the Muldenhütte in 1891 consisting of 6 cwt. of slag, 4 cwt. of roasted matte, and 4 cwt. of plumbiferous additions, which charge required 77 lbs of coke for smelting, 60 tons being put through every 24 hours.

The products of this smelting are work-lead with 0·4 to 0·7 per cent. of silver, and a matte known as copper-lead matte or slag matte, containing 30 per cent. of copper, 5 to 8 per cent. of lead, and 0·08 to 0·16 per cent. of silver, together with slag.

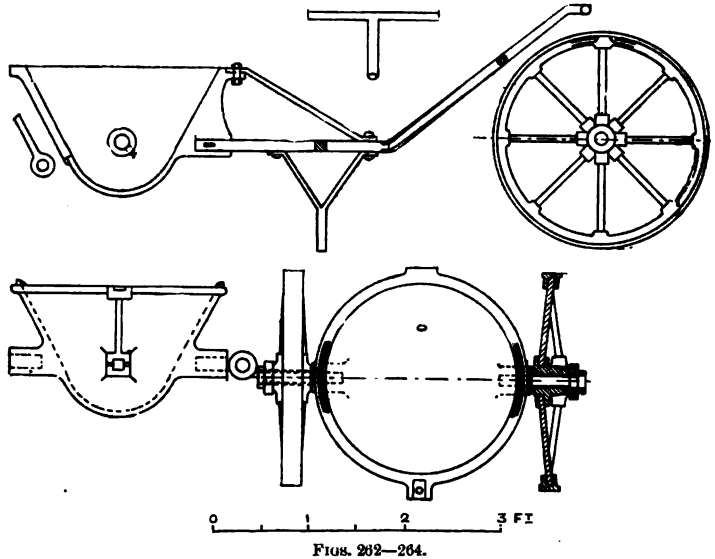
The work-lead is desilverised, the matte is roasted sweet, leaving a residue consisting chiefly of copper oxide which is treated with sulphuric acid to extract the copper, the residue being worked up for the silver it contains (*see* Silver).

The slags contain 0·0015 per cent. of silver and 1·5 per cent. of lead. The richer portions undergo a second slag smelting in the blast furnace, only with a smaller addition of plumbiferous materials, the charge at the Muldenhütte in 1891 being made up of 6½ lbs. of these additions and 6 cwt. of slag, requiring 77 lbs. of coke for smelting, 36 tons being treated in 24 hours. In addition to the work-lead produced, which goes to the desilverising process, a poor slag with 29 per cent. of silica, 37 per cent. of ferrous oxide, 9 to 11 per cent. of zinc, 1·5 per cent. of lead, and 0·009 to 0·0015 per cent. of silver is formed, which is thrown away.

In matte smelting a speiss is usually produced containing iron, lead, copper, nickel, cobalt and silver. This is roasted and then smelted with slags in a blast furnace, producing work-lead, matte and a second speiss. This is again roasted and smelted, and yields now a speiss with 0·05 per cent. of silver, 15 to 20 per cent. of nickel and cobalt, and 20 per cent. of copper, which is sold to the Saxon cobalt blue (smalt) works.

The cast iron slag pot runs on wheels and is provided with a tap hole 3½ inches from the bottom, strengthened by a flange from which a strengthening rib extends to the rim of the pot. The height of the hole from the bottom depends upon the amount of matte which accumulates in the pot.

In these slag pots the matte is allowed to settle to the bottom and thus to separate itself from the slag. The outer portions of the slag solidify, enclosing some matte, but the slag in the interior of this thin crust remains fluid and soon becomes free from entangled matte. When this is the case the still molten slag is tapped off by means of a steel rod, and the matte and solid portions of the slag remain behind. The tapped slag is thrown away, whilst the solidified shell



FIGS. 262—264.

and the matte both undergo a special slag smelting for the recovery of the lead, copper and silver contained in them. The character of the products obtained at the Omaha and Grant Smelting Works at Denver at the time of the author's visit may be cited as an example. Working in the manner just described, the waste slag contained 1¼ ozs. of silver per ton and 0·2 per cent. of lead, whilst the shell of slag remaining behind in the pots contained 4 ozs. of silver per ton. This was re-smelted, together with roasted matte and a small amount of a quartzose ore, producing lead and a matte rich in copper.

Care must also be taken in working the furnace to avoid the for-

mation of furnace bears and accretions. The separation of metallic iron, causing the production of iron bears, is caused both by the presence of an excess and of a deficiency of lime in the slag.

Deposits on the furnace walls, which are especially liable to occur during the smelting of zinciferous ores, are loosened or barred down, from above, after allowing the column of the charge to burn down low.

The temperature of the water running away from the jacket should not exceed 70°C. The volatilisation of lead is prevented as far as possible by the maintenance of a moderate temperature and by working with a dark furnace top. The lead fume is partly deposited amongst the cooler portions of the column of material in the furnace, and partly carried away with the escaping gases and condensed in suitable dust chambers, or other condensing arrangement, which should never be absent in any lead smelting works.

Products obtained by Smelting in the Blast Furnace.

The products of the roasting and reduction process are metallic lead, lead matte, slag, and in many cases speiss.

The lead, as a rule, is argentiferous, and if it does not contain too large an amount of impurity, it is submitted to the desilverising process and then is refined, or if impure it is refined before desilverising, and when necessary undergoes a second refining after that process. Lead free from silver is refined directly. The amount of silver and of other metals present in the lead varies within wide limits as the following analyses will show.

	Freiberg.	Mechernich.	Przibram.
Lead	95·088	99·513	97·359
Silver	0·47	0·021	0·423
Bismuth	0·019	...	0·007
Copper	0·225	0·133	0·11
Antimony	0·958	0·218	1·524
Iron	0·007	0·03	0·003
Zinc	0·002	0·006	0·001
Nickel	...	...	0·001
Sulphur	..	...	0·03

The lower portions of the pigs into which the lead is cast are richer in silver than the upper portions, and the portions at the centre of the top surface are the poorest in that metal.

The lead matte which is produced varies much in its character according to the amount of copper sulphide and of iron in the charge.

1 ton of ore is drawn from the furnace, so that in 24 hours 4 tons are roasted. The fuel used in roasting is a mixture of bituminous coal and lignite, and amounts to from 35 to 38 per cent. of the ore.

The ore is then smelted in a circular blast furnace, with 8 tuyeres, each $2\frac{3}{8}$ inches diameter, the blast pressure being $1\frac{9}{16}$ inches of mercury (page 368), together with limestone and ferruginous materials, the charge in the year 1881 being made up as follows :—

100	parts	of ore.
3·77	„	pig iron.
6·85	„	burnt pyrites.
5·05	„	calcite.
6·13	„	limestone.
0·45	„	spathic iron ore.
15·18	„	iron refinery slag.

Every 24 hours 22 tons of ore (31 tons of charge) are treated, 16·39 tons of coke and 155 bushels of charcoal being used to every 100 tons of ore.

The work-lead produced contains 0·44 per cent. of silver, and goes to the desilverising process. The matte, of which only a very small quantity is produced, is first roasted in stalls and then added again to the ore smelting charge. The slag containing less than 1·5 per cent. of lead and 0·0023 per cent. of silver, is thrown away, the richer slag being worked over again.

Smelting at Denver, Colorado.

The ores treated at the Omaha and Grant Smelting and Refining Company's Works, near Denver, are lead ores containing silver, zinc and copper, the average composition being 14 per cent. of lead and 60 to 75 ounces of silver per ton, 7 to 10 per cent. of zinc, and a smaller amount of copper. Rich galenas with less than 12 per cent. of zinc are smelted directly in blast furnaces without a previous roasting. The other ores are roasted in the reverberatory furnace, previously described (page 336), the mass being fused down at the end of the operation in the melting furnace attached to the roaster.

In 24 hours 11 tons of ore are roasted down to 8 per cent. of sulphur, 3 tons of coal being used, and 3 men being required in each shift.

The smelting of the roasted ore is carried on in the rect-

angular blast furnaces, described on page 376, the charge consisting of:—

250	lbs.	of roasted ore.
80	„	roasted matte from a previous operation.
70	„	oxidised iron ore from Leadville (with 5 to 10 ounces of silver per ton and 20 per cent. of manganese).
115	„	limestone.
180	„	slag.
120	„	coke.
20	„	charcoal.

In 24 hours 60 tons of charge, containing 40 tons of ore, are treated, the blast pressure being 1½ inches of mercury.

The products of the smelting are lead, with 300 to 400 ounces of silver and 3 to 4 ounces of gold per ton, 2 per cent. of copper, and 1 per cent. of antimony, this being refined and its gold and silver extracted; matte containing 6 per cent. of copper, 8 per cent. of zinc, 4 to 5 per cent. of lead, and 60 ounces of silver per ton; and finally slag with 1¼ ounces of silver per ton, 0·2 per cent. of lead, and 8 per cent. of zinc oxide. The matte is roasted in a *fortschaufelungs* furnace, 7½ tons being treated in 24 hours with the labour of 2 men per shift and a consumption of 3 tons of coal. The roasted matte is then smelted in a blast furnace (*spurofen*), together with the solidified richer outer portions or shells of the slag, the charge being made up of:—

600	lbs.	of slag shells.
300	„	roasted matte.
30	„	quartzose ores.
120	„	coke.
20	„	charcoal.

104 tons of charge are treated in 24 hours.

The lead obtained carries 600 ounces of silver to the ton and is desilverised; the matte contains 20 per cent. of copper, 4 per cent. of lead, and 100 ounces of silver per ton, and is treated further for these metals.

The slag is allowed to partially solidify in slag-pots, the poorer liquid portions tapped off and thrown away, and the solidified shells are added to the charge in either the ore or matte smelting.

Smelting in Spain.

The roasting and reduction process is carried on in the Spanish provinces of Murcia, Almeria and Jaen, where it has almost displaced the iron-reduction process formerly used. The ores, which in part contain considerable amounts of silver, are first roasted in single-hearthed reverberatory furnaces, and then smelted in blast furnaces. At some of the works (Mazarron, San Jacinto near Garrucha, Aguilas) large modern furnaces of circular section, cased with boiler plate, are in use, but most of the works employ the Castilian blast furnace of circular section with three tuyeres. The latter have almost displaced the draught furnaces which were formerly used, but, in addition, square, rectangular or round furnaces, with one or two tuyeres, are also employed. At Mazarron, where the smelting has recently been conducted in two large circular furnaces, work-lead with 0·12 to 0·14 per cent. of silver is produced; the lead from the smelting works near Carthagena contains 0·09 to 0·12 per cent. of silver.

THE IRON-REDUCTION PROCESS (*Niederschlagsarbeit*).

The iron-reduction process has for its object the production of lead from galena by the action of metallic iron, which at a certain temperature combines with the sulphur, forming ferrous sulphide.

The decomposition of lead sulphide by metallic iron only takes place at high temperatures, and is incomplete, because a portion of the ferrous sulphide which is produced combines with lead sulphide to form a double iron-lead sulphide or lead matte, which is the poorer in lead the higher the temperature at which the reduction is effected.

The iron is added either as metallic iron or in the form of some highly ferruginous material; if reverberatory furnaces or low blast furnaces with the ore charged in vertical columns are used, the iron must be employed in the metallic state. With taller blast furnaces charged horizontally, oxides and basic silicates of iron may with advantage be employed in place of the metal, the materials used being red and brown hæmatites, spathic iron ore, burnt pyrites, roasted lead matte, tap cinder or refinery slag. These are reduced to metallic iron in the furnace, and the iron formed reacts energetically with the lead sulphide.

The presence of other sulphides, or of arsenic and antimony compounds in the ore, is injurious, as they are reduced by the iron, and thus not only cause a waste of that metal, but also alloy with the lead and render it impure.

Copper and iron pyrites take up an additional amount of iron and increase the quantity of matte produced. Zinc blende is partly decomposed by metallic iron with the production of vapours of zinc, and passes partly into the matte and partly into the slag, thus giving rise to the same objections as in the roasting and reduction process.

Antimony sulphide is reduced by metallic iron with the formation of ferrous sulphide, the reduced antimony alloying with the lead. With excess of iron, a speiss consisting of an iron-antimony alloy is produced. When the charge contains arsenious sulphide, the arsenic as well as the sulphur combines with iron, and if present in large amounts, it gives rise to the formation of a speiss carrying with it copper, lead and silver.

The only sulphides without injurious influence on the iron-reduction process are those of copper and silver. Copper sulphide is decomposed by iron to a certain extent, but if it is present in excess it finds its way undecomposed into the matte. Silver sulphide is decomposed by both iron and lead and is found for the most part in the latter metal, a smaller amount being taken up by the matte. The silver is found in a considerably greater proportion as compared with the lead in the matte than in the separated metallic lead itself, and as there is no reason why the lead of the matte should take up more silver than the free lead, it is necessary to assume that a portion of the silver is taken up by the sulphide of iron in the matte; this is in accordance with the known fact that silver and iron sulphides readily combine one with another.

Of the other foreign substances employed in the process, lime, silica and the various lead-containing materials added, remain to be considered.

Lime, which is frequently present in the ores and is often purposely added in small amounts to the smelting charge, does not act directly on galena, or only to a very slight extent. [According to Berthier lime and carbon acting together partially reduce lead sulphide, forming calcium-lead sulphide and carbon monoxide according to the equation:—

$$2\,PbS + CaO + C = Pb + PbS.CaS + CO].$$

Lime, however, causes a separation of ferrous oxide from ferrous silicate and the separated oxide being reduced to metal by carbon effects a decomposition of the galena with the production of lead and ferrous sulphide. It also causes a separation of lead oxide from the slags at high temperatures. The slag itself is, as has already been mentioned, rendered less fusible by the addition of lime.

Silica is generally present in the ores and combines with the free bases present as well as with the bases of the basic slags added, forming silicates. Basic ores require an addition of silica or acid silicates to act as fluxes.

Lead oxide and materials containing lead oxide, such as litharge and old hearths and the mixture of oxides skimmed from the surface of the molten lead, react together with lead sulphide as in the other processes, forming lead and sulphur dioxide. Any lead sulphate in the roasted ores behaves in a similar way. The presence of these bodies is thus advantageous, as they replace a portion of the iron.

The quantity of iron necessary for reduction has been found in the Upper Harz to be 20 to 25 per cent. by weight of the galena smelted, the theoretical quantity being 23·43 per cent. If less iron be employed a smaller amount of lead is obtained in the free state as more goes into the matte. If an excess of iron be used, but little more lead is obtained, whilst the amount of silver in the matte increases.

The temperature in the iron-reduction process must be kept up to such a point that the matte contains not more than 10 per cent. of lead. For this purpose the charge must be so constituted as to possess the requisite fusibility, and the smelting must be properly conducted in suitable furnaces, which may either be reverberatory or blast furnaces.

The process if conducted in reverberatory furnaces requires the iron added to be in the metallic state, demands the consumption of a large amount of fuel, and is attended with a considerable loss of lead in the slag and by volatilisation. Blast furnaces are therefore generally employed, the use of reverberatory furnaces being quite exceptional. The former are not only cheaper but on account of their reducing capabilities allow of the iron being added as oxide or basic silicates.

The slags produced in the iron-reduction process must be sufficiently refractory to approach more nearly to bisilicates than to monosilicates, lime, ferrous oxide, magnesia and alumina serving as bases.

The lead matte produced in the process is roasted, whereby its iron sulphide is converted into oxide, and in this condition it is added to the ore charge in order that its iron may be available as a reducing agent. If it contains a large percentage of copper, or if its copper content has been brought up to a certain amount by repeated treatment with the ores in the furnace, then it is roasted several times over and smelted by itself. By this means the lead together with the greater portion of the silver contained in it are extracted, and the copper with a little silver forms a copper matte which is subsequently worked for its copper and silver.

The necessity for the employment of a high temperature and the impossibility of avoiding the formation of lead matte constitute the chief disadvantages of the iron-reduction as compared with other processes. The maintenance of a high temperature necessitates the consumption of a large amount of fuel and causes loss of lead by volatilisation, whilst the lead matte requires a series of operations to obtain the silver and copper contained in it, which operations are both costly and attended with further losses of metal. In spite of the advantages of the process, viz., the absence of any necessity for roasting the ores and the consequent smaller loss of silver, a good yield of lead and the possibility of obtaining any copper in the ore—it has on account of the above mentioned drawbacks been superseded in most places by the roasting and reduction process. As a separate process it is only rarely employed under exceptional local conditions as in the Upper Harz, whilst in other places, particularly in the United States, it is often used in conjunction with an oxidising smelting of the ores or with the roasting and reduction process.

The furnaces employed in the process are chiefly tall blast furnaces charged in horizontal layers. If low furnaces with the ore and fuel in vertical columns were used, the reduction of the iron from the oxide could not be effected, and in such cases the iron would have to be added in the metallic state. In the Upper Harz the lead matte produced in low furnaces contained 20 to 30 per cent. of lead, whilst in a tall furnace with the fuel and ore charged in horizontal layers it only contained 6 to 12 per cent. of lead.

The furnaces are constructed similarly to those used for the roasting and reduction process, furnaces of rectangular section being capable of smelting a greater quantity in a given time than circular ones. The ores should preferably be in a fine state of division as the decomposition, which demands intimate contact between the ore and the iron, thus becomes more complete. Slags must be charged with the fine ores in order to keep the furnace from being choked.

Charcoal or coke or a mixture of both is employed as fuel, and the pressure of the blast should be kept as low as possible in order to avoid the production of iron bears from the richly ferruginous material added.

The iron-reduction process in the Upper Harz.

At Clausthal and Lautenthal in the Upper Harz the iron-reduction process has reached a high state of perfection, the noticeable features of the process being the high percentage of silver obtained from the ores, the small amount of lead which is left in the

slag, the collection of the small percentage of copper present in the matte, and the employment of the roasted matte as a reducing agent in the furnace.

Recent analyses of the ores as they leave the dressing works, show them to have the following composition :—

Lead	50	to	74	per cent.
Silver	0·05	to	0·12	„
Copper	0·02	to	0·6	„
Zinc	0·3	to	7	„
Antimony	0·02	to	0·3	„
Iron	0·4	to	4	„
Sulphur	8·5	to	14·2	„
Alumina	0·07	to	1·5	„
Lime	0·2	to	1·4	„
Insoluble matter (quartz and silicates)	5·9	to	32·4	„

The average amount of quartz in the ore is 15 per cent.

The process was formerly conducted in well furnaces wider at the bottom than the top, with one or two tuyeres, the charge and fuel being introduced in vertical columns and metallic iron being employed as a reducing agent. Since the year 1835, endeavours had been made to substitute oxides and silicates of iron for the metal, but this change was only rendered possible in 1864 by replacing the older furnaces by Raschette furnaces and substituting coke for charcoal as the fuel, the latter having been used exclusively up to 1859. At first the material employed to furnish the necessary iron was the slag from copper smelting at Oker which contained 17 to 21 per cent. of silica, 66 to 70 per cent. of ferrous oxide and 1 to 2 per cent. of copper, the latter being obtained afterwards in the lead matte. More recently, roasted lead matte consisting mainly of iron oxides has with advantage been substituted for the slag.

At first the silica in the ores was fluxed by means of copper slags from the Lower Harz, and after these were exhausted, the residue from the wet copper extraction process at Oker was employed. This was obtained in the course of the extraction of copper from cupriferous pyrites which were submitted to an oxidising and chloridising roasting, the copper chloride being dissolved out by lixiviation. When the works at Oker ceased to employ this process, the necessary ferruginous material was obtained by using burnt pyrites from the sulphuric acid manufacture, tap cinder, hammer slag and brown hæmatites; these latter materials are still employed.

Both Raschette and circular furnaces are in use for smelting.

The newer furnaces are of the type of independent iron-cased Pilz furnaces, and have been modified by Kast to suit the iron-reduction process; two circular furnaces have also been built inside the retaining wall of a Raschette furnace (twin furnaces).

All the furnaces are arranged as well furnaces with fixed fore hearths on account of the refractory character of the charge with its content of zinc. The Raschette furnace has already been described and illustrated on page 370. One Raschette furnace at Clausthal measures 2 feet 10 inches by 7 feet at the tuyere level and 4 feet 6 inches by 7 feet at the throat, the distance between the two being 16½ feet. The tuyeres lie 3 feet above ground level, and the sump is 2 feet below the tuyeres. There are 12 tuyeres, 5 in each of the longer sides and one in each of the shorter ends. The Raschette furnace at Lautenthal is 22 feet high, measuring 3 feet by 7 feet 5 inches at the tuyeres and 4 feet 7 inches by 7 feet 5 inches at the throat with a distance between the two of 16 feet 5 inches. The tuyeres lie 20 inches above the lowest point of the well and 5 feet 6 inches above the floor level. There is the same number of tuyeres as in the Clausthal furnace, and they are similarly arranged.

The older circular furnaces at Clausthal are 18 feet 8 inches high from the working floor to the throat, having four tuyeres and being built of masonry. They are 3 feet in diameter at the tuyere level, and 4 feet 9 inches at the throat, the distance between the two being 15 feet 9 inches; the lowest point of the well lies 27½ inches below the tuyeres.

The new circular furnaces are provided with 4 or 5 tuyeres and are 3 feet in diameter at the tuyeres and 5 feet 5 inches in diameter at the throat, the height between the two being 19 feet and the distance from the tuyeres to the lowest point of the well 2 feet 6 inches, the several furnaces varying slightly from these dimensions. The tuyeres are 2⅜ inches in diameter, projecting 4 inches into the furnace and the pressure of the blast is equal to ¾ to 1 inch of mercury.

The arrangement of a four-tuyered furnace in use at Clausthal is illustrated in Figs. 265 and 266. *S* is the foundation stone, *s* the cast iron foundation plate, *y* a slag bed surrounded by brickwork *z*, *x* a clay layer topped by brickwork *w*, *v* a layer of quartz sand, and *u* the brasque hearth out of which the well is made. The brickwork *r* round the lower portions of the furnace is of ordinary brick for a height of 3 feet, and thence to a height of 3 feet 6 inches above the tuyeres is made of fire bricks. Water blocks *q* surround the water tuyeres *o*, *p* are the tuyere pipes, *l* is the blast main, and *m* is a flue for conveying the waste gases and dust into fume condensers. The

flue m is 20 inches in diameter and projects downwards into the furnace a distance of 31½ inches; n is the fore hearth, h the tap hearth, i the slag runner and b is the outer covering of iron plate lined with

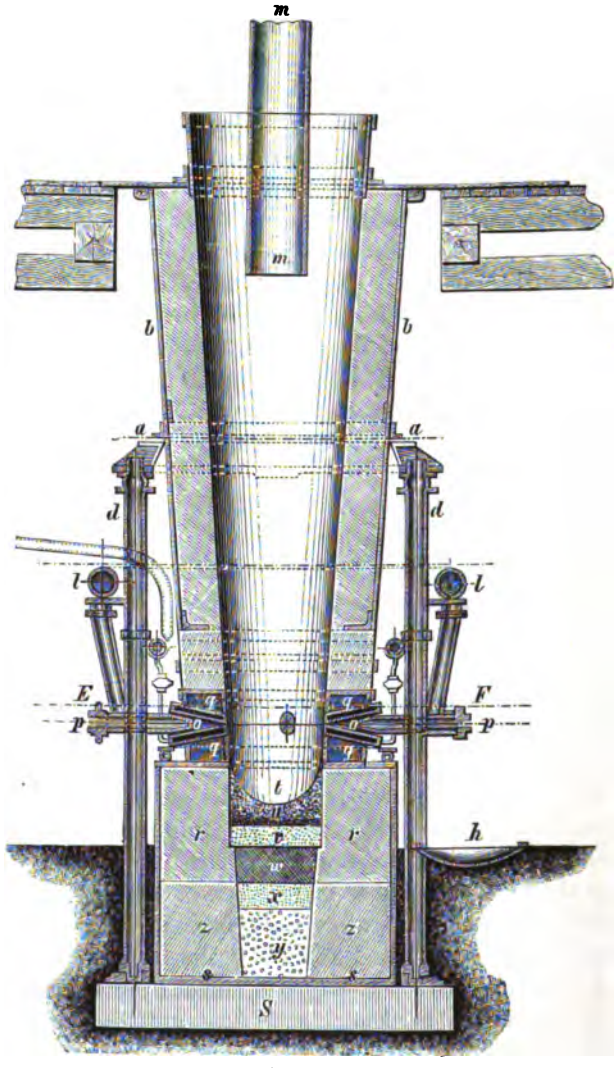


FIG. 265.

brickwork. A supporting ring a is fastened to b and is carried by the columns d which rest on the foundation S.

With suitable arrangements and proper management the productive capacity of the Raschette furnace can be made nearly

double that of the circular one, 3 to 3½ tons being smelted in the latter as against 6 to 6·8 tons per 24 hours in the former. The circular furnaces require the labour of 3 men per shift, 1 smelter, 1 charger and 1 slagwheeler; the Raschette furnaces that of 6 men, 2 for each duty.

As already mentioned the charge is made up of ore, a precipitating or reducing agent, a flux for the silica and earthy matter of the ore, together with some material, usually slag, to prevent the pulverulent ore from choking up the furnace. Any waste material containing lead or silver is also added, and at Clausthal the addition of limestone in small quantities has been recently practised. The composition of the charge varies with the nature of the material available as a flux for the

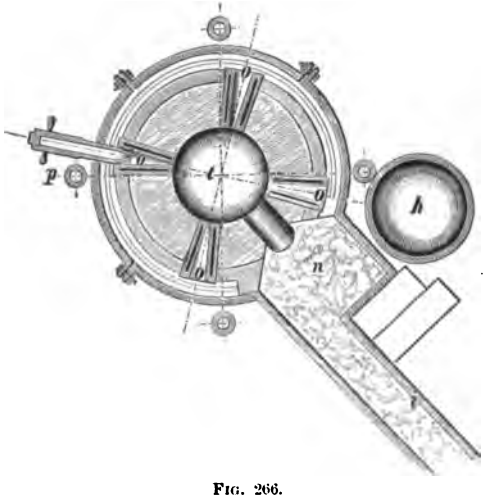


FIG. 266.

silica (burnt pyrites, tap cinder, hæmatite or mill cinder). At Lautenthal where the work-lead from Clausthal is desilverised and where consequently large amounts of argentiferous residues are produced, these are added in considerable proportions to the ore charge in order to obtain the metals contained in them. In the year 1888 the charges at Clausthal were made up as follows :—

100	parts	of ore.
50	„	roasted matte.
34	„	mill cinder.
28	„	slag from a previous operation.
70	„	matte slag.
8	„	limestone.

In the year 1890–1 the composition was as follows:—

100	parts	of ore slimes.
4·25	„	plumbiferous residues.
44·05	„	roasted matte.
33·48	„	mill cinder.
1·86	„	refinery slag.
1·31	„	spathic iron ore.
0·058	„	iron.
51·18	„	slag from matte smelting.
71·43	„	slag from ore smelting.
2·53	„	limestone.
0·77	„	fluorspar.

At Lautenthal in July 1893 the charge was made up as follows:—

Slimes	5	parts
Fume	0·3	„
Roasted matte	3	„
Burnt pyrites.	0·35	„
Litharge	0·5	„
Cupellation hearths	0·3	„
Roll scale	0·25	„
Slag from ore smelting	4·5	„
Slag from matte smelting	2·5	„
Limestone	0·5	„

The working of the process resembles that of the roasting and reduction process. The blast pressure employed is from ¾ to 1 inch of mercury. In 24 hours 6 to 6·8 tons can be smelted in the Raschette furnace or the twin furnace (see page 399) and 3 to 3½ tons in the single circular furnace. The consumption of fuel varies according to the composition of the charge and the character of the ores, from 35 to 43 per cent. by weight of coke, an average of 40 parts of coke being used for every 100 parts of ore.

Matte is produced in the proportion of 65 to 70 parts for every 60 parts of work-lead, though at Lautenthal, where a large amount of rich lead residues is added, more work-lead than matte is formed, *e.g.*, in the year 1892–93 for every 100 parts of work-lead 87·5 of matte were produced.

The work-lead and matte are tapped out together from the fore-hearth into a tap-hearth, whilst the slag continually flows away. As soon as the matte has solidified it is lifted out of the tap-hearth and the liquid lead remaining is ladled into moulds.

The work-lead contains on an average 0·14 per cent. of silver, and the following analyses by Hampe show its composition :—

	Clausthal.	Lautenthal.
Lead	98·2944	98·96475
Copper	0·1862	0·2838
Antimony	0·7203	0·5743
Arsenic	0·0064	0·0074
Bismuth	0·0048	0·0082
Silver	0·1412	0·1421

	Clausthal.	Lautenthal.
Iron	0·0064	0·0089
Zinc	0·0028	0·0024
Nickel	0·0023	0·0068
Cobalt	0·00016	0·00035
Cadmium	traces	traces

This work-lead is desilverised at Lautenthal. The lead matte from the iron-reduction process contains on an average 7 to 15 per cent. of lead, 3 to 8 per cent. of copper and 0·02 to 0·0325 per cent. of silver. At Clausthal the lead matte produced in 1884–85 had the following average composition :—

	Per cent.
Lead	12·91
Copper	3·50
Silver	0·03
Antimony	0·31
Zinc	3·29
Manganese	0·19

	Per cent.
Nickel and Cobalt	0·09
Iron	48·35
Lime	0·75
Silica	1·49
Magnesia	0·05
Sulphur	28·81

Lead matte also contains oxygen, according to Hampe,[1] as the following two analyses of Clausthal lead mattes produced in 1878 or 1877–78 will show :—

	I	II
Sulphur	23·921	25·65
Lead	15·500	12·44
Iron	42·940	48·64
Copper	6·295	3·49
Antimony	0·120	0·13
Silver	0·044	0·035
Zinc	6·000	4·31
Manganese	traces	traces
Nickel	0·26	0·11

	I	II
Silica	1·56	1·22
Alumina	0·77	1·51
Lime	0·156	0·51
Magnesia	0·024	0·05
Potash (K_2O)	0·17	0·13
Soda (Na_2O)	0·28	0·10
Sulphur trioxide	0·22	not estimated
Oxygen	1·50	2·03
	99·76	100·355

The amount of sulphur in the matte, after deducting the amount combined with the copper as Cu_2S and with the silver as Ag_2S, is not sufficient to form normal sulphides with the metals present. Iron and lead must therefore either exist as free metals dissolved in the matte or else as lower sulphides, the existence of which, as already mentioned, has not been proved.[2]

The lead matte produced at Clausthal in the year 1886–7 contained on an average 11·008 per cent. of lead, 3·81 per cent. of copper and 0·021 per cent. of silver, 80·92 per cent. of the lead in the original charge being obtained as work-lead and 10·14 per cent. in

[1] Chemiker-Ztg, 1892, 16, No. 28.

[2] Schnabel, *Allgemeine Hüttenkunde*, page 9.

the matte. Of the silver originally present, 87·01 per cent. was found in the work-lead and 13·22 per cent. in the matte. The method of treating this matte is given on a subsequent page.

The slags, as regards their content of silica, lie between mono- and bi-silicates, more nearly approaching the latter; the slags from Clausthal in recent times have contained somewhat less silica than was formerly the case. The composition of the older slag from Clausthal was as follows:—

	Per cent.		Per cent.
Silica	37·908	Manganous oxide	1·02
Ferrous oxide	32·695	Potash	0·419
Ferrous sulphide	1·823	Soda	1·013
Barium sulphate	1·508	Nickel and cobalt oxides	0·038
Alumina	8·32	Copper	0·08
Lime	5·416	Silver	0·0007
Magnesia	1·302	Antimony	0·059
Zinc oxide	3·948	Sulphur	0·031
Lead oxide	3·896	Phosphoric acid	0·708

A more basic slag from Clausthal produced in the year 1889–90 had the following composition:—

	Per cent.		Per cent.
Silica	31·58	Phosphorus pentoxide	0·83
Barium sulphate	1·34	Zinc oxide	6·90
Baryta	1·34	Manganous oxide	0·71
Lead	2·45	Lime	4·90
Copper	0·16	Magnesia	0·11
Ferrous oxide	40·29	Sulphur	2·63
Alumina	7·20	Silver	0·0007 to 0·001

By assay, the slags contain 0·5 per cent. of lead. They are thrown away, except such portions as may be required to keep the charge open in ore smelting and as a flux in matte smelting.

THE SMELTING OF LEAD MATTE

As has already been mentioned, the lead matte after roasting serves as a flux and as a source of iron in the iron-reduction process. Every time that it is employed in this way its percentage of copper increases and at last it reaches a point at which the work-lead begins to take up considerable quantities of this metal from it, so that the copper percentage must not be allowed to exceed a certain amount. This is effected by periodically withdrawing portions of the matte from the process and replacing this by fresh matte, the withdrawal being made as soon as the amount of copper in the matte reaches 12 per cent., when it is worked up by itself for the copper it contains. In actual practice at the Clausthal works about one fifth

of the matte produced in smelting is being continually withdrawn from the process in this way, and separately treated for copper matte.

The matte produced is first roasted, no matter whether it is being worked up for its copper, or whether it is going to be put back into the iron-reduction furnace. At Clausthal, the roasting is carried on in heaps, to the great injury of the surrounding country on account of the action of the gases evolved; at Lautenthal and at the Altenau works the matte is roasted in shaft furnaces.

Before roasting, the matte is allowed to lie exposed to the air, whereby it crumbles and becomes friable and is easily broken into small pieces. By a single roasting, in heaps, the sulphur in the matte is not reduced to the requisite extent and it has to undergo 4 or even 5 separate roastings before the sulphur is reduced to the required 6 per cent. After each firing the contents of the heap are sorted, the well roasted parts put on one side, whilst the imperfectly roasted portions and the outside parts go to form a new heap. In the first roasting about one third of the matte will be sufficiently roasted, the remaining two-thirds having to undergo a second roasting.

The heaps are built up on a layer of brushwood and coal or billets of wood. The capacity of the heaps varies from 150 to 300 tons according to the amount of matte available and the degree of roasting desired. The first firing lasts 2 to 3 months, the later ones require a shorter period, and the entire contents of a heap usually require roastings lasting altogether about 6 months before they are ready for the next operation.

At Lautenthal, the matte is roasted in shaft furnaces or kilns of which six are grouped together. They have vertical walls and are 13 feet 10 inches high, 7 feet 6 inches broad and 8 feet 4 inches deep. From the floor two sloping saddle-shaped pieces crossing each other rise to a height of 2 feet, and the roasted material is withdrawn at four places, through two doors at the front and two at the back. The raw matte is mixed with roasted matte in order to prevent it being fritted together, three parts of once-roasted matte being mixed with four parts of raw matte. Each kiln is capable of roasting 2·2 tons of matte (both raw and roasted) every 24 hours, the roasted material containing 8 per cent. of sulphur, whereas the pyrites kilns formerly in use at Lautenthal only reduced the sulphur down to 13 per cent. The gases evolved from the roasting kilns contain 5 to 6 volumes per cent. of sulphur dioxide and are used for sulphuric acid making.

The roasted matte, or such portion of it as is not required as an addition to the ore smelting, is now smelted, together with slag from

ore smelting, in a blast furnace with 1 or 2 tuyeres in the back wall arranged as a well furnace, the products being work-lead, copper matte and slag. At Clausthal, the furnace is 22 feet 8 inches high, circular in section, 4 feet 7 inches in diameter at the throat and 2 feet 7½ inches at the tuyere level which lies 2 feet 3 inches above the hearth. There is a single tuyere 2½ inches in diameter which projects 8 inches into the furnace.

The charge consists of 100 parts of matte and 100 to 140 parts of slag from the ore smelting, and in 24 hours 5·69 tons of roasted matte are smelted with a coke consumption of 1·61 tons, each ton of coke smelting 4·94 tons of matte or 12·19 tons of charge. Two men are required for each shift, one smelter and one charger. From every 100 parts of roasted matte 8 parts of work-lead and 15 to 16 parts of copper matte are obtained. The work-lead contains 0·22 per cent. of silver, and is refined before desilverising, because it is not as suitable for the zinc desilverising process as the lead from the ore smelting on account of the copper in it. The matte contains:—

Lead	8·01 per cent.
Copper	12·29 „
Silver	0·035 „
Iron	45·62 „
Zinc	3·36 „
Sulphur	21·8 „

The lead matte, which has been treated over again in the ore furnace to obtain the copper in it, leaves the furnace richer of course in that metal. At Lautenthal for instance, the matte from the iron reduction process contains 7 to 8 per cent. of copper, 10 to 17 per cent. of lead, and 0·03 per cent. of silver. This is smelted in a blast furnace 9 feet 10 inches high, of trapezoidal section, with two tuyeres and a blast pressure of ¾ to 1 inch of mercury. The distance between the tuyeres and the throat is 8 feet, the back wall is 2 feet 6 inches long at the tuyere level, and the front one 20 inches, a space of 40 inches separating the two walls. The throat is almost circular, of 2 feet 9½ inches diameter, and the nozzle of the tuyeres measures two inches in diameter. To every 3·6 parts of matte, 4·2 parts of ore slag are added; in 1893 equal weights of each were being used; every 24 hours 3·6 tons of matte or 7·8 tons of charge are smelted with a coke consumption of 1·11 tons.

The products are work-lead with 0·16 to 0·24 per cent. of silver, and matte with 7 to 8 per cent. of lead, 0·03 per cent. of silver, and up to

20 per cent. of copper. The slag contains 1·55 to 2 per cent. of lead, the composition of the Clausthal slag being as follows:—

	Per cent.		Per cent.
Silica	24·91	Nickel }	0·13
Lead	1·55	Cobalt }	
Copper	0·90	Zinc oxide	6·56
Silver	0·0022	Manganese oxide	0·75
Antimony	0·20	Magnesia	0·38
Ferrous oxide	51·85	Lime	4·25
Alumina	4·50	Sulphur	3·86
Phosphoric anhydride	0·69	Soda (Na_2O)	0·33
		Potash (K_2O)	0·51

The matte is roasted and then smelted, producing a matte richer in copper, and some work-lead. The matte roasting is carried on, as previously described, at Clausthal in heaps, and at Lautenthal in kilns.

The smelting of the roasted matte mixed with slag from the ore smelting, is effected in blast furnaces. At Clausthal 140 parts of ore slag are added to every 100 parts of matte; at Lautenthal equal amounts of each are used. From every 100 parts of roasted matte 5 to 7 parts of lead are obtained and 22 to 27 parts of copper matte. The work-lead contains 0·24 per cent. of silver and is softened before desilverising; the matte contains 28 to 40 per cent. of copper, 6 to 13 per cent. of lead, and 0·07 to 0·08 per cent. of silver. A matte of this kind from Clausthal contained:—

Lead	13·00	Iron	21·88
Copper	35·72	Zinc	2·23
Silver	0·08	Sulphur	19·49

The slag from this second matte smelting at the Clausthal works had the following composition:—

Silica	27·21	Nickel and cobalt	0·06
Barium sulphate	1·11	Zinc oxide	0·24
Lead	2·25	Manganese oxide	1·07
Copper	1·39	Magnesia	0·52
Silver	0·0012	Lime	5·46
Antimony	0·08	Soda (Na_2O)	0·31
Ferrous oxide	54·56	Potash (K_2O)	0·64
Alumina	0·85	Sulphur	2·34
Phosphoric anhydride	0·85		

This slag, like that from the previous smelting and the one produced in the subsequent smelting, is a monosilicate and is added to the ore smelting.

The matte produced in this second smelting is then worked up for its copper. It is roasted and smelted in blast furnaces arranged like the previously described *spuröfen*. This roasting and smelting is repeated three or four times; no work-lead is produced as a rule,

but the copper matte and the black copper contain lead. The roasting is effected in heaps or in Wellner's stalls, as roasting in kilns is difficult on account of the easy fusibility of the matte. The smelting furnace has the same dimensions as that used in the first matte smelting, and the various kinds of roasted matte are smelted with an admixture of ore furnace slag in the proportion of 100 to 120 parts of slag to every 100 of roasted matte.

At Clausthal, in this third smelting, 100 parts of roasted matte yield 10 parts of black copper and 46 parts of copper matte, 1·55 tons of matte, or 3·49 tons of charge being smelted in 24 hours using 0·47 tons of coke. The black copper contains 30 per cent. of lead, which is separated from it by liquation; the matte has the following composition:—

Lead	9·06	Iron	19·98
Silver	0·075	Zinc	1·59
Copper	42·30	Sulphur	17·89

And the slag from this operation contains:—

Silica	17·43	Manganous oxide	0·49
Lead	1·47	Zinc oxide	4·30
Copper	1·90	Cobalt and nickel	0·27
Silver	0·0015	Lime	2·00
Antimony	0·09	Magnesia	0·39
Ferrous oxide	62·14	Potash (K_2O)	0·57
Alumina	5·87	Soda (Na_2O)	0·33
Phosphoric anhydride	0·43	Sulphur	1·47

The matte is now submitted to 4 or 5 alternate roastings and smeltings, whereby black copper and a matte much richer in copper are obtained. In many cases the fifth and sixth operations are combined on account of the small quantities of matte available. At Clausthal, from 100 parts of roasted matte, the following amounts were obtained:—

at the 4th operation	24·7	parts of	black copper	and	38·5	parts of	matte
,, 5th ,,	18·9	,,	,,		59·5	,,	,,
,, 6th ,,	17	,,	,,		56·3	,,	,,

The black copper from the sixth operation, produced at Clausthal in 1883 had the following composition:—

Copper	69·37	Iron	1·15
Lead	24·45	Cobalt, Nickel	1·64
Silver	0·28	Zinc	0·41
Antimony	0·39	Sulphur	1·60
Arsenic	0·16		

At Lautenthal, by the combined fifth and sixth operations (known there as the second and third working of the copper-matte), 62 parts of black copper and 31 parts of matte are obtained from every 100

parts of roasted matte. The black copper contains 0·24 to 0·30 per cent. of silver, 10 to 15 per cent. of lead, and 75 to 78 per cent. of copper, and the matte contains 0·1 per cent. of silver, 3 per cent. of lead and 75 to 78 per cent. of copper.

The composition of the mattes produced at Clausthal from the fourth and fifth workings in 1884 and from the sixth operation in 1885 is given below:—

	IV.	V.	VI.
	1884	1884	1885
Lead	6·32	3·88	2·36
Silver	0·06	0·035	0·02
Copper	58·10	59·86	52·18
Iron	11·10	12·24	19·82
Zinc	0·96	0·75	0·59
Sulphur	20·15	20·78	20·20

And the composition of the slags from Clausthal from the same operations in the same years was as follows:—

	IV.	V.	VI.
	1884	1884	1885
Silica	17·06	18·97	21·49
Lead	1·02	0·92	0·81
Copper	1·88	1·58	1·66
Silver	...	...	...
Antimony	0·34	0·20	0·32
Ferrous oxide	65·08	61·84	59·68
Alumina	5·36	6·47	8·55
Phosphoric anhydride	0·45	0·47	0·79
Manganous oxide	0·56	0·50	0·52
Zinc oxide	2·55	2·90	2·02
Cobalt and nickel	0·34	0·54	0·38
Lime	2·32	2·27	2·56
Magnesia	0·24	0·47	0·41
Potash (K_2O)	0·63	0·77	0·75
Soda (Na_2O)	0·41	0·53	0·47
Sulphur	1·02	0·92	1·55

THE COMBINED ROASTING AND REDUCTION AND IRON-REDUCTION PROCESS

The iron-reduction process is usually combined with the roasting and reduction method of smelting, especially when a portion of the ore is rich in silver and is in consequence smelted direct without

previous roasting. The combined processes are also used when owing to lump ores being roasted in heaps or stalls, the percentage of sulphur is not reduced sufficiently. In all these cases ferruginous fluxes are added to the charge in order that iron may be reduced in the furnace for the decomposition of the sulphides still left in the charge. The process of smelting does not essentially differ from the smelting in the roasting and reduction process and it is conducted in similar furnaces. A similar method of smelting is in use at Altenau and Andreasberg in the Harz (see the section on Silver), and at the Victor-Friedrichs works near Alexisbad.

At the Victor-Friedrichshütte the so-called raw smelting ores that are treated, are ores containing limestone and spathic iron ore and 20 per cent. of lead, blendes with 50 per cent. of lead, and jigged ore with 20 per cent. of lead, these being smelted in pieces of 1 to 1¼ inches cube in Pilz furnaces, together with roasted galena with 40 per cent. of lead. The roasting of the lead ores is conducted in a long-bedded calciner (*fortschaufelungsofen*), 35 feet long, 6 feet 10 inches broad, five charges of half a ton each being in the furnace at once, and the roasting being carried far enough to sinter the mass together. In 24 hours 4 tons of ore are treated with a fuel consumption of 0·4 ton of coal, 35 cubic feet of wood and 7 cubic feet of *cinders*, the sulphur in the ore being reduced to 2 per cent.

The smelting is conducted in a Pilz furnace arranged as a crucible furnace (page 368), the charge consisting of:—

30	per cent.	raw ores.
20	„	roasted ores.
40	„	slag from a previous operation.
10	„	limestone.

In 24 hours about 20 tons of ore are smelted with a blast-pressure of 1⅛ to 1½ inches of water and a consumption of 12 per cent. of the weight of the charge in coke. The matte produced forms 80 per cent. by weight of the work-lead obtained, and the work-lead has the following composition:—

Copper	0·2674	Sulphur	0·0784
Antimony	0·8296	Zinc	0·0023
Lead	98·4296	Iron	0·0355
Silver	0·235	Nickel, Cobalt	traces
Arsenic	0·0264		

The matte contains about 25 per cent of lead, 2 per cent of copper and 61 per cent. of iron, and the slag, which is a monosilicate, has the following composition:—

Silver	0·001	Lime	3·9
Silica	28·9	Magnesia	1·1
Alumina	11·2	Lead sulphide	1·4
Manganous oxide, Ferrous oxide	48·8	Zinc sulphide	6·0

The work-lead is either first desilverised or is cupelled direct. The matte is roasted in kilns and stalls and then smelted in Pilz furnaces, together with those portions of the slag, which, on account of the lead in them, have not been thrown away. To the charge for this smelting, various bye-products containing lead are also added, as for instance old cupellation hearths, litharge, and lead dross, together with certain kinds of ores (fluxing ores) containing some copper, silver and lead. At one time the composition of the charge was as follows:—

60 per cent. slag.
10 „ spathic ore.
10 „ pyritic slimes.
10 „ roasted matte.
10 „ lead dross or similar plumbiferous material

Every 24 hours, 40 tons of charge are smelted, the coke used forming 7 to 8 per cent. by weight of the charge, and the blast pressure being equivalent to 11 to 12 inches of water.

By this smelting a work-lead is produced, a clean slag, and a matte containing about 5 per cent. of copper, and 12 to 15 per cent. of lead. This is re-roasted and again added to the slag smelting until it contains 12 to 15 per cent. of copper and it is then worked up with suitable fluxes for its copper, silver and lead.

At the Julius and Sophien works (see page 385), where the ores are roasted in heaps and only imperfectly desulphurised, the smelting operation is really a combination of the iron-reduction with the roasting and reduction process, the latter however being the chief process; the necessary iron is furnished mainly by the iron oxide present in the roasted ores.

In the United States pure argentiferous galenas are usually added in a raw state to the roasted ores, and if the silver present amounts to more than 100 ounces per ton they are nearly always smelted raw, and often when it falls below this amount. Roasted lead matte serves as a reducing agent or if this is worked up by itself, ores containing iron oxide or pure hæmatite take its place. The method of working and the arrangement of the furnaces resemble those employed for the roasting and reduction process.

THE COMBINATION OF THE IRON-REDUCTION PROCESS WITH THE SMELTING OF OXIDISED ORES

The working up of lead carbonate with the sulphide by the iron-reduction process is chiefly carried on when the carbonate is present in the ores in excess. This was the case for a considerable time in many of the works in the Western States of America though the process was also formerly used even when galena was in excess. At the present time at these works, ores with more than 15 per cent. of sulphur, whether existing as pyrites, arsenical sulphides and zinc blende or as galena, are usually first roasted unless they contain an unusually large amount of silver. As previously mentioned, ores containing more than 100 ounces of silver per ton are not roasted.

All ores, however, in which the lead carbonate predominates over the sulphide are smelted without a preliminary roasting. Sulphides containing a large amount of silver, as well as ores with a small percentage of sulphur, are mixed in suitable proportions with oxidised ores. The latter usually carry sufficient iron oxide to act as reducing agents for the iron-reduction process. The lead matte produced in the process is added to the charge after being roasted, so that its oxide of iron is available as a reducing agent. The actual conduct of the process is precisely similar to the smelting operation of the roasting and reduction process. It is employed at various works in Colorado (The Pueblo, Colorado and Philadelphia smelting works) and also in Nevada and Utah.

Mixtures of lead carbonate and galena are also smelted in Tasmania at the Zeehan and Dundas Smelting works near Zeehan. The carbonate contains 10 per cent. of silica, 5 to 10 per cent. of manganese and 25 per cent. of lead, whilst the galena is very pure and contains up to 150 ounces of silver to the ton. The furnaces used are rectangular, water-jacketed, American ones, measuring 3 feet 4 inches by 11 feet 4 inches at the tuyere level. The height from the working floor to the throat is 20 feet and there are 16 tuyeres. In 1892 the ore mixture contained the following constituents:—

Silica.	7 to 8 per cent.
Ferrous oxide.	21 to 24 „
Manganous oxide	4 to 6 „
Lead.	38 to 41 „
Sulphur.	2·6 „
Silver	25 to 32 ounces per ton.

Every 24 hours 80 tons of charge were smelted, and the slag produced contained 30 per cent. of silica, 40 per cent. of ferrous oxide and 20 per cent. of lime.

In the Spanish provinces of Murcia and Almeria, galena is smelted together with lead carbonate and brown hæmatite, argentiferous hæmatites being also often added. In this way the galena is reduced by the iron formed by the reduction of the iron oxides. The furnaces are draught furnaces or Castilian blast furnaces and the products are work-lead and matte; the latter was formerly thrown away, but is at present roasted and again added to the ore charge. Most of the Spanish works at the present day however employ the roasting and reduction process.

THE SMELTING OF LEAD CARBONATE

Lead carbonate gives off carbon dioxide when heated to 200° C, and the oxide so formed is reduced by carbon or carbon monoxide at a red heat, so that the metallurgical treatment of carbonate ores resolves itself into a smelting in reverberatory or blast furnaces with the addition of a reducing agent and a flux for the gangue.

Reverberatory furnaces are only rarely used, as the slags produced in them are rich in lead, requiring a subsequent treatment in blast furnaces; consequently they are only employed when very pure ores are to be smelted. The furnaces are provided with a well or sump, and the ore is heated on the sloping hearth together with coke, charcoal, lean coal or brown coal, in a reducing flame and with constant stirring. The reduced lead drains into the well and the residual slag is smelted in blast furnaces.

Lead carbonate is however usually smelted in blast furnaces, which are used for this purpose in Southern Spain, the Western States of America and in New South Wales. The ore is smelted together with suitable materials to serve as fluxes for the gangue, and as this generally consists of silica, lime or ironstone is used; the slag produced in the process is also used both as a flux and to keep the charge open.

The furnaces used resemble those employed for the roasting and reduction process. In a rectangular American furnace measuring 36 by 60 inches at the tuyere level, 48 tons of carbonate with 40 per cent. of lead and free from zinc, were smelted in 24 hours, or 18 tons of a similar carbonate containing 18 to 20 per cent. of lead.

When the ore deposits were first discovered at Leadville, Colorado, the ores smelted were pure carbonates containing large quantities of

silver, but at present the ores contain galena in addition or consist exclusively of sulphides; the lead present in the ores has also decreased from an average of 20 per cent. down to 12 per cent. The silver in the Leadville carbonates was present partly as chloride and partly as native silver, the amount of silver present varying from 0·06 to 2 per cent.

At the works of Berdell and Witherell at Leadville, ores containing 30 per cent. of lead and 300 ounces of silver per ton were smelted in rectangular water-jacketed blast furnaces 8 feet 6 inches high from hearth to throat, and 4 feet by 2 feet 7 inches in section, having 5 tuyeres, each 2½ inches diameter, situated two on each side and one in the back wall. The blast pressure was $1\frac{3}{16}$ inches of mercury. The charge consisted of 2 cwt. 23 lbs. of ore, 46 lbs. of slag, 26 lbs. of ferruginous ores containing some silver and gold, 27 lbs. of coke and 27 lbs. of charcoal, ten tons of ore being smelted in 24 hours. The products were work-lead with 0·9 per cent. of silver, matte with 1 per cent. of arsenic and a little antimony, and slag with 0·003 to 0·006 per cent. of silver.

At the present time the greater part of the carbonates smelted in the Western States come from Mexico, and contain on an average 20 per cent. of lead. At the time of the author's visit to the Philadelphia works near Pueblo in Colorado, Mexican ores were being smelted in addition to those from Colorado and Utah, the ores averaging 38 to 40 ounces of silver per ton. The charge was made up so as to contain 13 per cent. of lead, and the work-lead obtained carried from 160 to 300 ounces of silver per ton. The furnaces were rectangular and water-jacketed, having a total height of 22 feet, the height from the tuyere level to the throat being 15 feet, and measuring 3 feet 6 inches by 10 feet at the tuyere level, widening 10 inches on either side up to the boshes. Such a furnace smelted 60 to 70 tons of carbonate ores in 24 hours. The slag produced contained ½ per cent. of lead and ½ an ounce of silver per ton.

At the works of the Consolidated Kansas City Smelting and Refining Company at El Paso in Texas, carbonates from the Sierra Mojada in Mexico, containing 25 per cent. of lead and 22 ounces of silver per ton, are smelted together with argentiferous ores free from lead but rich in iron and manganese oxides, from Tombstone, Arizona. The furnaces are of the rectangular American type, water-jacketed, with automatic taps. They have 13 tuyeres, each 4 inches in diameter, and measure 10 feet by 3 feet 6 inches at the tuyere level. From the tuyeres to the throat the height is 17 feet, and the blast pressure is 17 inches of water.

The charge is as follows :—

900	lbs.	of ore.
350	„	limestone.
300	„	slag from a previous operation.
1550	lbs	of charge.
200	„	coke.
40	„	charcoal.

40·5 tons of ore, 15·5 tons of limestone and 13·5 tons of slag are smelted in 24 hours, the average lead content of the charge being 11 to 13 per cent., and the average silver content 40 ounces per ton. Every 24 hours 4 tons of work-lead with 200 to 300 ounces of silver per ton and 0·5 to 1·5 ounces of gold are produced, and 1·5 tons of matte with 80 to 100 ounces of silver per ton. The slags produced contain 0·5 to 1·5 per cent. of lead, and 0·75 to 1·5 ounces of silver per ton, together with 32 per cent. of silica, 38 per cent. of ferrous oxide and 20 per cent. of lime in addition to zinc oxide, alumina, sulphur, lead, &c.

The work-lead is desilverised; the matte is first roasted in stalls, then in reverberatory furnaces, and is then smelted with quartzose ores containing copper and silver, the second matte so produced being worked up at the Argentine works in Kansas City for copper and silver.

At the present time at Broken Hill, New South Wales, argentiferous lead carbonates are smelted together with argentiferous ores containing silica and kaolin, and but little carbonate. The silver present in these ores exists principally as chloride and as native silver with a little iodide and bromide. The principal veins from which these ores are derived change in character as they go deeper down, altering into a mixture of galena and blende, so that the carbonate smelting will probably cease in time as the surface deposits are exhausted. The furnaces in use at the Broken Hill works are oblong American ones with cast iron water jackets and Arents's syphon tap; they measure 5 feet by 9 feet 4 inches at the tuyere level, and there are 12 tuyeres, 5 in each of the longer sides and 1 at each short end of the furnace. Figs. 267 to 270 show the construction of the furnace.

At the largest of the works, those of the Broken Hill Proprietary Co., the ores smelted in the year 1891–92 contained 15 to 18 per cent. of lead and 32 to 39 ounces of silver per ton, and were made up of 51·5 per cent. of carbonate ores, 47 per cent. of siliceous, clayey

and ferruginous ores, and 1·5 of argentiferous iron ores containing some lead.

This charge of ore was mixed with 32 per cent. of limestone and 3·1 per cent. of ironstone, 50 tons of mixed ores being smelted in each furnace in 24 hours, the fuel used being 18 per cent. of coke and 2·8 per cent. of charcoal, 7 workmen being required for each furnace in each shift. In that year (1891–92) 246,907 tons of ore were smelted, yielding 39,390 tons of lead and 9,269,022 ounces of silver.

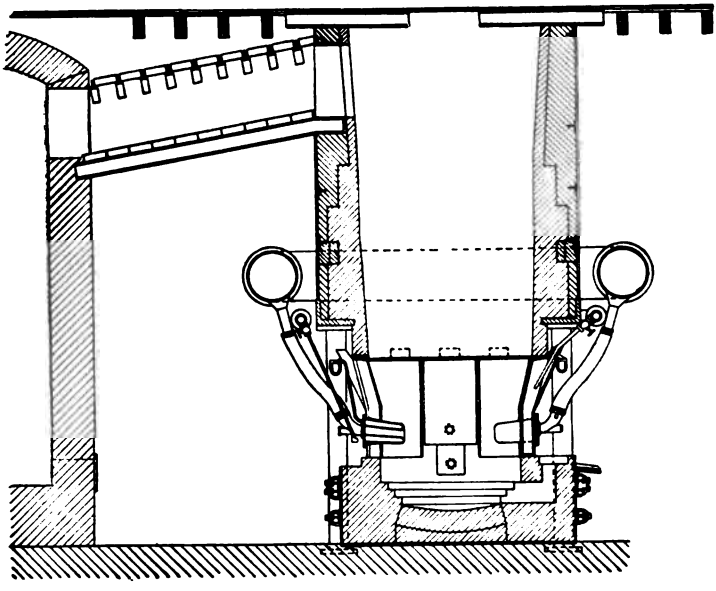


Fig. 267.

Part of the Broken Hill ores are smelted on the sea coast in South Australia (Dry Creek near Adelaide, and Port Pirie), similar methods being employed. Part of the work-lead produced is desilverised in Australia, but the bulk of it is sent to Europe for further treatment.

THE SMELTING OF LEAD SULPHATE

Lead sulphate only rarely occurs in sufficient quantity to allow of its being worked by itself for the lead it contains, and it is usually smelted in admixture with other ores.

If it has to be worked alone, reverberatory furnaces are the most suitable. If galena is available it is added in such quantity that the

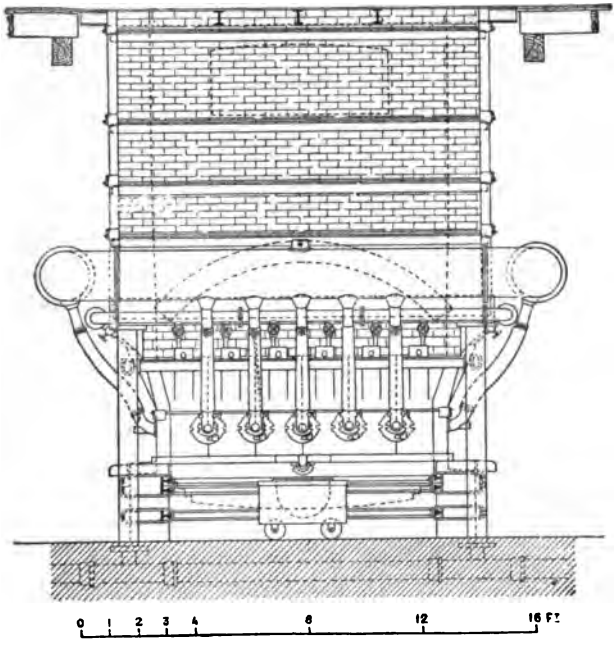


FIG. 268.

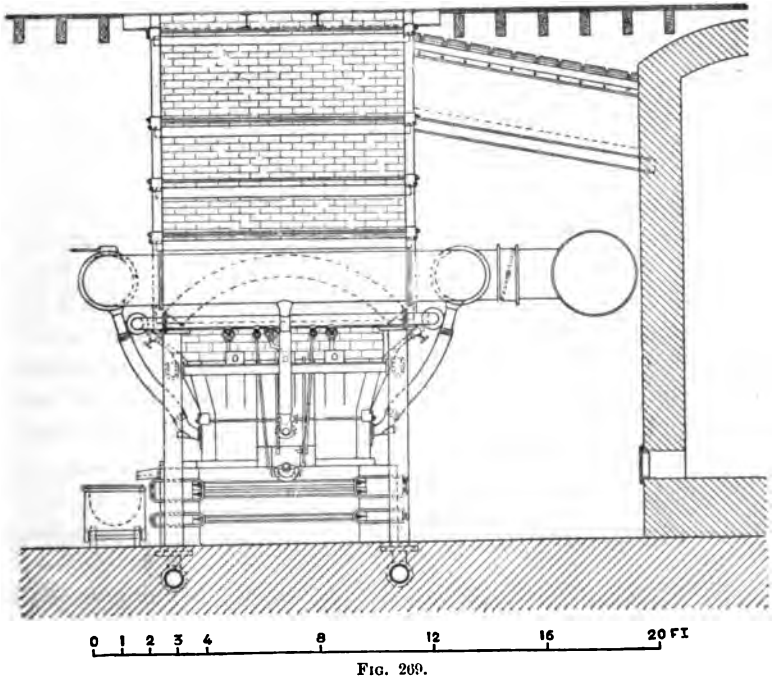


FIG. 269.

proportion of sulphide to sulphate present is the same as in the air-reduction process, lead and sulphur dioxide being produced by their interaction. If however galena is not available, a certain amount of coal is added to the charge in order to reduce a portion of its sulphate to sulphide, the two compounds afterwards mutually reacting, producing lead and sulphur dioxide. A residue is always left, which must be further treated in blast furnaces.

Another method of working lead sulphate consists in first melting it with quartz in reverberatory furnaces whereby lead silicate is formed; this is then treated in blast furnaces with limestone and ferruginous materials in the same way as the lead silicate produced in the roasting and reduction process. Lastly, lead sulphate may be smelted in reverberatory furnaces with carbon and iron, or with carbon and oxides of iron or basic iron silicates in blast furnaces. By this means the lead sulphate is first reduced to sulphide by the carbon, and this is then reduced by the iron which has itself been formed by the reduction of the ferruginous material, forming lead and lead matte. Schnedermann (Percy-Rammelsberg, p. 297) proposed to use reverberatory furnaces for smelting lead sulphate with 67 per cent. of calcium carbonate, 37 per cent. of fluor-spar and 12 to 16 per cent. of coal, the calcium sulphate formed being fluxed by the fluor-spar, and lead being produced.

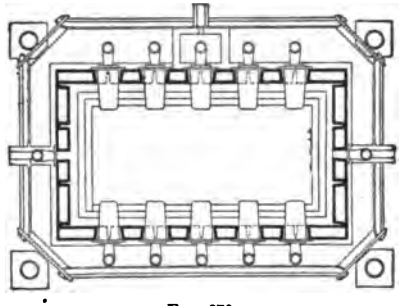


FIG. 270.

At Bagillt in Flintshire, Australian lead ores containing 57·5 per cent. of lead sulphate and 0·96 per cent. of silver were smelted in quantities of 25 cwt. with $1\frac{1}{2}$ cwt. of small coal, $\frac{3}{4}$ cwt. of pig iron, and $\frac{1}{2}$ cwt. of burnt pyrites in reverberatory furnaces, such a charge being worked off in 8 hours. The products were work-lead with 3·98 per cent. of silver and some gold, and a small amount of lead matte ($\frac{3}{4}$ cwt.) containing 13·5 per cent. of lead, 5 per cent. of copper and 0·08 per cent. of silver; this on roasting and smelting yielded work-lead and copper matte.

THE SMELTING OF PLUMBIFEROUS METALLURGICAL PRODUCTS

These are obtained during lead smelting, the refining of the lead, and the subsequent desilverising, and consist principally of residues

from the air-reduction process, lead mattes, slags, furnace accretions and deposits, dross and skimmings from various operations, flue dust, litharge and old cupellation hearths.

Residues from the air-reduction process

These contain lead oxide, sulphate, sulphide and silicate. They are smelted in blast furnaces by the roasting-and-reduction process, or this combined with the iron-reduction method. In the latter case the sulphide is reduced by metallic iron added to the charge, or by iron reduced in the furnace from ferruginous materials in the charge.

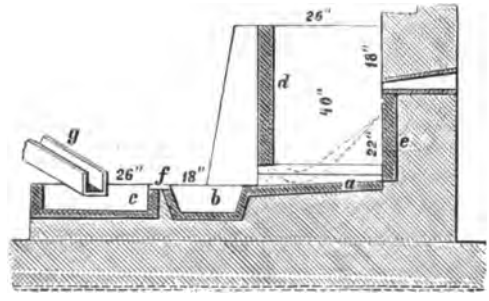


FIG. 271.

In some of the English works a slag hearth or low blast furnace 3 feet high, built up of cast iron plates and furnished with a single tuyere, is employed. This is arranged as a *spurofen*, *i.e.* a furnace in which the molten products are not allowed to accumulate but run off as they are formed; the hearth bottom is made of cinders well stamped down, and there is a forehearth in which are two pots or wells of cast iron, one for the lead, the other for the slag. The slag flows over from the first into the second where it is granulated by a stream of cold water so that any entangled shots of lead can easily be separated from it; the lead is ladled out from the well or run from it into a tap hearth.

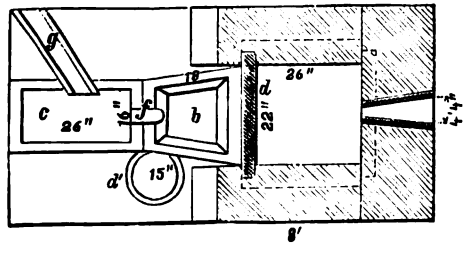


FIG. 272.

The general arrangement is shown in Figs. 271 and 272 where *d* is the front and *e* the back wall, *a* the hearth plate, *b* the lead well, *c* the slag well, *g* the spout conveying water for breaking up the slag and *d'* the tap hearth. The hearth, lead well, and slag well, are covered with a layer of cinder. At Keld Head about 4 tons of residues are worked up in such a furnace in 6 hours.

It is better however to employ taller blast furnaces like those

described as being used for the roasting and reduction process. As an instance the working up of the residues from the Tarnowitz process at Friedrichshütte may be cited.

The furnace used is similar to that employed in the roasting and reduction process with a blast pressure of 22·5 mm. of mercury, and the charge consists of :—

2·5 to 3·0	tons of	residues.
0·15	„	old hearths.
0·05	„	materials containing some lead.
4·0	„	rich slags.
0·3	„	calcined lead matte.
1·0	„	iron finery slag.
0·2	„	limestone.
Total ... 8·20	tons	

Every 24 hours, 25 tons of charge (7·5 to 8 tons of residues) are smelted, coke to the amount of one twelfth of the weight of the charge being consumed.

Lead mattes and slags

The working up of lead mattes has already been described under the headings of the roasting and reduction and iron-reduction processes. Slags are added to the ore smelting charge and the charge for matte smelting, but if they are present in such quantities as to necessitate separate treatment, like the slags from the roasting-and-reduction process at Freiberg and the Laurium Mountains slag in Greece, then they are most advantageously smelted in blast furnaces.

At Freiberg the rich slags are smelted in Pilz furnaces with the production of work-lead and copper matte as described on page 389.

The Laurium slags were formerly smelted in slag hearths with lime and ironstone, but modern four-tuyered circular furnaces with water jackets are now used.

These slags, which date back to the time of Solon and Xenophon and partly to the time of Strabo (B.C. 66), possess the following composition according to Diez :—

Silica	27·5	to 35·7	per cent.
Lead oxide	8	to 15·36	„
Zinc oxide	2	to 9	„
Ferric oxide	14	to 25	„
Lime	10	to 28	„
Magnesia	1	to 3	„
Alumina	3	to 9	„

When using circular blast furnaces, the slag produced from this slag smelting contains 0·5 to 1 per cent. of lead; 6·6 parts of charge require 1 part of coke, and 1·9 parts of coke are used for every unit of lead obtained.

Furnace accretions, dross, furnace residues and flue dust

By furnace accretions are meant the masses which are found adhering to the furnace walls, consisting of half melted portions of the charge together with volatilised lead sulphide and portions of the masonry lining of the furnace; dross and furnace residues are impure slags and solidified plumbiferous masses obtained in cleaning the hearths of the furnaces. These bodies are added to the ore smelting charge, either with or without previous dressing.

Fluedust.—In all lead smelting works arrangements must be made for the condensation of the metals and metallic compounds which are volatilised during the smelting as well as of those portions of the ore charge which are mechanically carried away in the flue gases, (see Schnabel "Allgemeine Hüttenkunde"). Unfortunately many works are still serious offenders in these matters, such arrangements being either not in use or defective in character.

The condensed matter or flue dust consists chiefly of lead sulphate, lead oxide, metallic sulphides and portions of the charge and fuel, and, where zinc compounds are present in the charge, considerable amounts of oxide of zinc. The composition of various flue dusts is given in the following table:—

	Pueblo Colorado)	Upper Harz.	Ems. I.	Ems. II.	Freiberg.
Lead	—	34·8	60·48	67·04	35·2
Lead oxide	37·65	18·0	—	—	—
Lead silicate	—	2·9	—	—	—
Zinc	—	1·0	3·17	4·22	5·28
Zinc oxide	5·32	1·5	—	—	—
Cadmium oxide	—	—	—	—	1·30
Arsenic	—	3·0	0·24	0 ·16	28·3
Antimony	—		0·42	0 ·31	—
Silver	0·04	—	—	—	—
Iron	—	—	0·003	·003	—
Ferric oxide	24·98	1·0	2·12		
Alumina	1·31	4·5		1·0	1·57
Lime	5·26	—	1·15	0·61	1·01
Magnesia	—	—	—	—	0·25
Silica	8·63	12·3	—	—	6·19
Sulphur	2·53	7·8	6·22	5·42	—
Sulphur trioxide	1·61	2·8	14·78	14·07	3·38
Carbon dioxide	11·20				
Water					
Carbon		2·5	8·0	5·8	1·17

Flue dust is usually mixed with clay or lime, and added to the ore smelting charge in blast furnaces. It is also added by itself to the ore charge smelted in reverberatory furnaces by the air-reduction method (see the Tarnowitz process). In the works of the Lower Harz it is first treated with dilute sulphuric acid on account of the high percentage of zinc oxide present which the sulphuric acid dissolves. This flue dust has the following composition:—

Zinc oxide	28·90 per cent.
Lead oxide	20·26 „
Copper oxide	0·72 „
Silver	0·07 „
Lime	0·45 „
Sulphur	5·43 „
Insoluble residue	18·14 „
Loss on ignition	9·58 „

After extraction with sulphuric acid the residue is added to the ore smelting charge and the liquors are worked up for zinc sulphate. If the flue dust has to be treated alone it must first be agglomerated by means of some binding material or else compressed into bricks. Bituminous substances answer best as the binding material, such as bituminous schist or coal tar. At the Mansfeld copper works, flue dust with 14 per cent. of lead is obtained and this is mixed with crushed *kupferschiefer*, pressed into bricks, and then burnt, together with cupriferous schist; after this treatment it is smelted with rich iron slags in blast furnaces (at Eckarthütte), producing a work-lead with 0·3 to 0·4 per cent. of silver.

Smelting of Bye-products Obtained in Cupellation Processes.

In the Pattinson and Parkes's processes for the concentration of the silver contained in work-lead and in the cupellation process, certain bye-products are obtained which are worked up for lead by a reducing smelting.

These products are cupriferous and argentiferous scums and the old hearths of the cupellation furnace (*schlicker*, *abzug*, *abstrich*, and *glätte*).

Schlicker are the scums which form on the surface of cupriferous lead when it is melted for the purpose of being desilverised; they contain metallic lead, oxides of lead and copper, and a certain amount of silver. They are first submitted to a process of liquation in order to extract some argentiferous lead, and the residue is added to the ore

smelting, or better still to the matte smelting charge. If they are obtained in such quantities as to necessitate a separate smelting as, for instance, when more desilverising is being done than ore smelting, or where desilverising alone is practised, then they are smelted in blast furnaces with pyrites or galena, the products being work-lead and cupriferous lead matte, which latter is roasted and smelted for copper matte in blast furnaces.

Litharge (*glätte*) is produced during the oxidation of lead for the purpose of extracting the silver, as in the cupellation process. The hearth of the furnace in which this operation is conducted absorbs a portion of the litharge, and is also treated for its lead and silver. In most works at the present day the argentiferous lead is submitted to a process of concentration, with the production of a small amount of a highly argentiferous lead and a much greater quantity of poor lead. Only work-leads, which are extremely impure, chiefly those containing large amounts of copper and which cannot consequently be treated by the concentration process, are directly cupelled.

Litharge, produced in the cupellation of rich argentiferous leads, contains some silver and is consequently added to the ore smelting if argentiferous lead ores are being treated, or if ore smelting is not being carried on, it is smelted, together with the saturated hearth, for work-lead. Litharge obtained in the cupellation of poor lead is as a consequence poor in silver and is either sold as litharge or reduced, yielding market lead. The term "freshening" (*Frischen*) is applied to the smelting process by which the litharge is reduced.

Old hearths are treated in just the same manner as the litharge. If rich in silver they are added to the ore smelting, or smelted together with litharge, for work-lead, and if poor in silver are smelted for market lead.

The "freshening" or reduction of the litharge can be conducted in hearths, reverberatory furnaces or blast furnaces. Reduction in hearths is only an imperfect process on account of the large loss of metal attending it and the excessive consumption of fuel, and is consequently only rarely used. A special form of hearth is known as the Siberian litharge reduction hearth, in which the fluid litharge is allowed to flow uninterruptedly out of the cupellation furnace through a mass of glowing charcoal placed in a sort of box in front of the litharge outlet. The air for the combustion of the charcoal enters by the same opening from which the reduced lead flows. Such an arrangement is economical as regards fuel, but it renders the working of the cupellation hearth more difficult and exposes the workers more to the fumes of lead; a residue is also left which requires to be smelted

in the blast furnace. This Siberian reduction hearth is used at Schemnitz in Hungary and in the Altai Mountains.

The litharge is usually reduced in reverberatory furnaces; by suitably regulating the temperature, excessive loss of lead by volatilisation is prevented, and foreign metals do not alloy with the lead, but in this case also rich lead residues are produced, which require to be smelted in blast furnaces.

The furnaces are arranged similarly to those used in the air-reduction process, being built with sloping hearths of brasque with an outlet like the Carinthian furnace or with a well. The reduced lead flows out continually in the first case, or is periodically tapped if the latter arrangement be adopted. In many cases the ordinary German cupellation furnace is used for this purpose, a tap hole being provided for running off the collected reduced lead.

The litharge is not intimately mixed with carbon, but the two are charged in alternate layers, a lean coal being the form of carbon generally used. After charging, a feeble fire is maintained and the temperature raised to dull redness, the mass being stirred from time to time, the fire being increased towards the end of the operation in order to separate the last portions of the lead from the residue; the residue is then withdrawn and a fresh charge inserted. The residue consists of lead oxide, carbon, impurities contained in the lead, the ash of the coal, and portions of the hearth, and is either worked up alone or with other lead products in blast furnaces, or if antimony is present, it is smelted for hard lead. The scums which form on the lead after it is withdrawn from the furnace are put back again with the litharge.

At Deebank in North Wales according to Rivot 4 charges of litharge of 3 tons each were reduced in 24 hours in a furnace 11 feet 6 inches long and 7 feet 6 inches broad, 1·4 tons of fuel being required for heating, and 1·2 tons of coal as a reducing agent. The yield of lead was 90 per cent., and the residue formed 3 per cent. of the weight of the litharge, and contained 40 to 50 per cent. of lead. At the Pertusola works near Spezzia 30 tons of litharge are reduced in 24 hours with a yield of 90 per cent. of the contained lead.

The reduction of litharge in blast furnaces is best effected in the modern forms, resembling those used for ore smelting and arranged as crucible furnaces the reduction in *spurōfen* having been abandoned. The litharge is mixed with slag from a previous operation in order to protect the reduced lead from the action of the blast, and coke or charcoal is used as fuel.

The products are lead and slag, the lead from the reduction of

litharge poor in silver being comparatively impure as compared with the market lead from the Parkes and Pattinson desilverising processes. This is shown by the following determinations of the foreign bodies present in the lead from the litharge reduction at the Upper Harz smelting works :—

	Lautenthal (Streng).	Clausthal (Hilgenberg).
Copper	0·07	9·081
Antimony	0·240	0·023
Iron	0·005	0·0086
Zinc	0·015	0·013

The slags are rich in lead (8 to 50 per cent.) and are consequently returned to the process and they also mechanically enclose some unreduced litharge ; the dross (*bleidreck*) formed on the surface of the lead after tapping is also added again to the charge.

In the Upper Harz, where in former years lead was directly cupelled without any previous concentration of the silver and the litharge produced was poor in silver, the reduction of the litharge was carried out on a large scale. At the present time only the small amount of lead produced in matte smelting is cupelled directly, the ordinary work-lead being previously desilverised ; consequently a very much smaller amount of poor litharge is produced and this is reduced, together with bye-products from Parkes's process, or else added to the ore smelting charge.

The reduction was effected in sump furnaces 16 feet 5 inches high, with one tuyere, working with an air pressure of $\frac{9}{16}$ to $\frac{5}{8}$ of an inch of mercury. To every 100 parts of litharge 11·5 parts of slag from the same smelting were added, and 9 tons of litharge were reduced every 7 hours, the coke used forming 11 per cent. of the weight of the litharge.

In the Lower Harz 10 tons of litharge were smelted by 2 tons of coke in a sump furnace, with two tuyeres, working with a blast pressure of $\frac{3}{8}$ inch of mercury.

At Freiberg the litharge is reduced in eight-tuyered Pilz furnaces, one furnace reducing 65 tons of litharge mixed with 33 per cent. of slag in 24 hours with a coke consumption of 4·5 to 5 tons. The slags obtained carry 10 per cent. of lead.

The hearths of the cupellation furnaces, which are made of a mixture of lime and clay, of natural marl, of bone ash, or of cement, absorb lead oxide and a certain amount of silver. They are broken up and the pieces added to the charge in the smelting of argentiferous ores, mattes or argentiferous litharge, in blast furnaces. It is only rarely that the hearth is smelted by itself and then it is most conveniently treated in blast furnaces, together with a flux.

Scums (*abzug*) form upon the surface of the impure work-lead, when it is first melted in the cupellation furnace, and consist of impurities which were mechanically entangled in the lead, particularly matte, of copper and work-lead, and of lead oxide and oxides of easily oxidisable metals. These scums are added to the ore or matte smelting to obtain the silver, lead and copper contained in them, or if produced in large amounts they are smelted, together with pyrites, yielding work-lead and a matte, which is subsequently worked up for the copper, silver, and lead contained in it.

At Freiberg, where the work-lead contains tin, the tin is found in the difficultly fusible scum first formed on the surface of the lead in the cupellation furnace. This is worked, according to Plattner's process, to form a tin-lead alloy,[1] the composition of the scum being as follows :—

Lead oxide	70·35 per cent.
Stannic oxide	12·53 „
Antimonic oxide	12·50 „
Arsenic oxide	4·73 „
Cupric oxide	0·61 „
Silver	0·25 „

It is first smelted in a reverberatory refining furnace with 5 per cent. of carbon as a reducing agent, the products being work-lead and an *abstrich* free from silver but containing 11·5 per cent. of tin and 14·5 per cent. of antimony. This *abstrich* is then smelted in the Pilz furnace with 15 per cent. of slags and 25 per cent. of coke, yielding lead containing 11·8 per cent. of tin, 10·3 per cent. of antimony, and 3·5 per cent. of arsenic, and this impure lead then undergoes an oxidising melting in a reverberatory furnace, yielding an *abstrich* rich in tin and a lead containing 15 per cent. of antimony. The *abstrich*, known as first tin powder (*erster Zinnpuder*), is smelted in blast furnaces with twice its weight of slag from a previous operation or with slags from the first operation and 60 per cent. of its weight of coke, again yielding impure lead (*zweites Zinnfrischblei*). This lead is again submitted to an oxidising melting in a reverberatory furnace and the products are antimonial lead, with 18 per cent. of antimony, 1 per cent. of arsenic, and 0·5 per cent. of tin, and a second tin powder, containing 44 to 50 per cent. of lead, 24 to 27 per cent. of tin, 11 to 13 per cent. of antimony, 0·48 to 0·95 per cent. of copper, and 0·95 to 2·72 per cent. of arsenic. The second tin powder is smelted in a furnace 7 feet 6 inches high, provided with a

[1] *Jahrbuch für das Berg- und Hüttenwesen in Sachsen*, 1883.

well and two tuyeres, in charges of about 28 lbs., together with 5½ lbs. of coke, yielding an impure lead with 33 per cent. of tin, 14 per cent. of antimony, and 1 per cent. of arsenic. The resulting slag contains considerable quantities of tin, both mechanically mixed as well as combined, and it is smelted without any addition, except 20 per cent. of coke, in a blast furnace for "slag tin-lead" of much the same composition as the other tin-lead. The slag produced contains 5·3 to 8·8 per cent. of stannic oxide and is rejected.

Abstrich is a mixture of lead oxide and antimoniate, together with oxides of the common metals present in the lead, and is produced in the refining or softening of argentiferous lead before desilverising the same, or in the refining of lead free from silver, or of lead which has undergone the process of desilverising.

The *abstrich* is as a rule submitted to a preliminary process of liquation in order to separate as much of the lead as possible, and at the same time to concentrate the antimony contained in it, and then if it contains sufficient antimony it undergoes a reducing smelting with the production of a lead-antimony alloy, or hard lead. If the *abstrich* is poor in antimony, it is added to the ore or matte smelting.

The liquation of the *abstrich* is conducted in reverberatory furnaces with brasque hearths, in lead refining furnaces, or in the cupellation hearth. It is either melted directly on the hearth or, as in the Upper Harz, laid on a layer of wood placed on the hearth, and it is also mixed with some coal, which serves, together with the layer of wood, for the reduction of the oxide. The fluid lead is first run off and as soon as this has been ladled out of the tapping hearth, the molten *abstrich* is also tapped off or else the entire contents are tapped at once, the heavier lead sinking to the bottom of the tap hearth, and the lighter *abstrich* overflowing on to the working floor. The liquated argentiferous lead is then usually cupelled.

At Lautenthal, in the Upper Harz, the liquation of the *abstrich* produced in the cupellation of the lead from matte smelting, is conducted in a German cupellation furnace with brasque hearth and tap hole and tapping hearth. The brasque is made of four parts of coke and one of clay slate, and a charge of four tons of *abstrich* is placed on a layer of brushwood previously put on the hearth. The fireplace is provided with an air blast, coal and brushwood being used for fuel, the liquation of the four tons taking ten hours. The molten lead is first tapped out and after this has been ladled out of the tapping hearth the molten *abstrich* is allowed to flow in. In a particular instance 16 tons of *abstrich* yielded 9·7 tons of liquation residue and 6 tons of lead, the fuel used consisting of 100 faggots of

brushwood and 3·6 tons of coal, together with a ton of coke for the brasque hearth. In another case at Lautenthal from 7,275 lbs. of *abstrich* with 86 per cent. of lead, 1,322 lbs. of lead, and 5,511 lbs. of liquated *abstrich* were obtained.

At Freiberg, the argentiferous *abstrich* is mixed with 20 per cent. of coal and then liquated in the furnace used for refining the work-lead before desilverising. Seven tons of *abstrich* are treated in 24 hours with a consumption of 15 per cent. of coal and 5 per cent. of brown coal, 1·9 tons of lead, and 3 tons of liquation residue containing 10 to 14 per cent. of antimony being obtained.[1]

The "freshening," or reduction of the *abstrich*, is carried out in furnaces similar to those used in reducing litharge. Owing to its difficult fusibility this is best effected in one of the modern forms of blast furnace into which the *abstrich* is charged, together with slags from a previous operation and slags from the matte and ore smelting. In the reducing smelting, the antimony contained in the *abstrich* combines with the lead, and the antimony reduced from the lead antimoniate present is also taken up by the lead which is present in excess.

The percentage of antimony in the hard lead obtained varies a good deal according to the percentage of antimony in the materials from which it was derived; usually it is from 10 to 20 per cent., but occasionally rises to as much as 40 per cent. In many cases the hard lead is still further purified by melting in pots and passing steam through, as in the Upper Harz, or by poling.

In addition to the liquated *abstrich* there are other materials which are worked up for antimonial lead, namely, bye-products obtained in refining the desilverised work-lead, litharge from the cupellation of the lead obtained in matte smelting, dross from the casting of pig lead, and scums and dross from the tap hearths and pots in which the hard lead is collected.

At Lautenthal the process of smelting for hard lead is carried on in a well furnace, with one tuyere, worked with a blast pressure of about an inch of mercury. The charge was at one time made up as follows:—

4·50	tons	of liquated *abstrich* from the cupellation of matte lead.
60·25	,,	,, *abstrich* from the refining of desilverised lead.
10·00	,,	,, scums from the purification of hard lead in cast iron pots.
4·50	,,	,, *abstrich* from the hard lead in the tap hearth.
4·76	,,	,, scums from pig lead (the 2nd quality of market lead).
12·70	,,	,, slag from ore smelting.
25·15	,,	,, slag from a previous operation.
1·95	,,	,, roasted copper pyrites.

[1] *Jahrbuch für das Berg- und Hüttenwesen im Konigreich Sachsen*, 1883.

By a consumption of 12·75 tons of coke, 64 tons of lead and 4·5 tons of scums from the tapping hearth are obtained, and 10 tons of drosses are treated in 24 hours.

The hard lead which is produced by this process is melted in cast iron pots in quantities of 11 to 12 tons at a time. Four hours after charging, the dross (*schlicker*) forming on the surface is skimmed off, and then steam is passed through the molten metal the temperature of which is not much above 400° C. for 10 to 15 minutes, after which the purified lead is ladled into moulds. A certain amount of copper is always added to the hard lead in the pot. From the 64 tons of hard lead obtained as above, 50·2 tons of antimonial lead and 13 tons of dross or scum are obtained with a consumption of 3 tons of coal and 40 faggots of wood.

The average percentage of antimony present in refined hard lead is 17 to 19, and the silver content 0·001 to 0·002 per cent.

The composition of the refined antimonial lead from the Upper Harz is as follows :—

	1890-1.	1891-2.	1892-3.
Lead	81·71	82·44	82·08
Antimony	17·69	16·90	17·34
Copper	0·62	0·68	0·62

At Freiberg,[1] the *abstrich* from the refining of the argentiferous lead previous to desilverising is liquated in reverberatory furnaces, with 2 per cent. of coal for reduction, and then smelted in a Pilz furnace, the liquated *abstrich*, which contains 10 to 14 per cent. of antimony, being mixed with an equal weight of poor lead slags or of slags from a previous operation. In 24 hours, 22 to 23 tons of *abstrich* are smelted with a consumption of 0·9 ton of coke, and the production of 3·5 tons of hard lead containing 18 per cent. of antimony, 3 per cent. of arsenic, and 0·4 per cent. of tin. This hard lead is melted in cast iron pots in quantities of 15 tons and poled for 4 hours, the entire purification process lasting 7 hours. Every 100 parts of crude hard lead yield 85 of refined hard lead and 15 parts of dross; 3 per cent. of brown coal and 3·5 per cent. of bituminous coal are used as fuel. The refined hard lead contains 15 per cent. of antimony, 2·5 per cent. of arsenic, and 0·3 per cent. of tin.

The drosses, or scums, &c. (*schlicker*), obtained in refining the hard lead are submitted to a process of liquation in the ordinary lead softening or refining furnace, by which means a quantity of hard lead (72·5 per cent.), containing 13·2 per cent. of antimony, 2·8 per cent. of arsenic, and 0·1 per cent. of tin, is obtained. On account of the con-

[1] *Jahrbuch für das Berg- und Hüttenwesen in Sachsen*, 1883.

siderable amount of tin in it, the residue remaining after the liquation is added to the reduction process for tin *abstrich* (see page 426). The rich lead slags from the *abstrich* reduction are smelted separately in blast furnaces for hard slag lead, which, like the hard lead from the *abstrich* reduction, is purified by melting in iron pots and poling.

In the first slag smelting, the slags produced are too rich in lead and antimony to be thrown away, and they are consequently smelted, with an addition of 10 per cent. of limestone, in blast furnaces, yielding a waste slag containing 2·5 per cent. of antimony and slag lead. In this process 25 tons of slag are smelted in 24 hours, with a consumption of 20 per cent. of coke. The various bye-products obtained in refining lead are cupriferous scums, liquation residues (*Saigerdörner*), drosses and lead ashes, and zinciferous lead oxides. The scums and liquation residues are added to the charge in ore and matte smelting, or smelted separately with an addition of pyrites, the products being work-lead and matte. Argentiferous scums undergo a liquation process previous to smelting, by which means argentiferous lead and a liquation residue are produced. *Abstrich* and all antimonial bye-products are treated in the manner previously described, in order to obtain an antimonial hard lead. Zinciferous oxides are added to the charge in smelting ores poor in silver, or else worked up separately, together with basic iron slags, or with the addition of poor litharge. When these oxides consist of a finely divided mixture of zinc and lead oxides and shots of metallic lead, as is the case when they are produced in the dezincifying of the desilverised lead by means of steam, they are submitted to a washing process before being reduced; the zinc oxide thus washed out contains a good deal of lead oxide, and is saleable as a pigment.

Lead ashes (*bleidreck*) are added either to the ore smelting charge or the smelting of oxides poor in silver, or to the "freshening" of poor litharge.

The Refining of Lead

The lead obtained by any of the processes previously described contains in most cases other elements as impurities, and if they are present in any quantity they exert an injurious influence on the properties of the market lead. These elements are copper, arsenic, antimony, zinc, iron, bismuth, tin and sulphur, and their removal, when they exceed a certain proportion, is necessary before the lead is

sent to market. This purification of the lead is also necessary in the case of work-lead which is to be desilverised, as the presence of copper, antimony, arsenic, and, in the case of Parkes's process, of nickel and cobalt, interferes with the proper conduct of the desilverising process.

Lead which has been desilverised by zinc, no matter whether it had undergone a previous purification or not, must still be refined to free it from the zinc and other impurities taken up in the process. Purification processes must consequently be divided into three classes:—

1. The refining of lead free from silver.
2. The refining of argentiferous lead.
3. The refining of desilverised lead.

The method of refining depends upon the nature and amount of the impurities which have to be eliminated, and provided they are similar in each instance, precisely similar methods would be used for each class of lead.

The elements commonly present as impurities in lead, viz., arsenic, antimony, tin, zinc, nickel, cobalt, iron and sulphur, possess a greater affinity for oxygen than lead itself, and can in consequence be got rid of by an oxidising fusion. Copper and bismuth alone possess a smaller affinity for oxygen than lead, and consequently cannot be completely eliminated by oxidation. Copper, however, forms with lead a copper-lead alloy, less fusible than lead alone, and this separates out, when the lead is melted, as a crust or scum (*schlicker, abzug*), or it remains behind in the solid form, as a liquation residue (*saigerdörner*) when the lead is liquated. Zinc also possesses the power of extracting copper from cupriferous lead, forming with it an alloy which separates out on the surface of the molten metal as it cools.

Bismuth cannot be separated from lead by any of the above methods. In the concentration of argentiferous lead by Pattinson's process it goes with the silver into the rich silver lead, and is subsequently obtained in the litharge from the cupellation furnace. But in other cases where the lead is free from silver, or where the zinc process of desilverising is employed and the lead is not cupelled and the litharge reduced, the whole of the bismuth remains in the lead. The presence of even large quantities of bismuth up to as much as 1·9 per cent., which only rarely occurs, does not, according to Junge of Freiberg, interfere with the malleability of the lead, and it is there-

fore scarcely necessary to consider processes for the separation of bismuth from lead unless the extraction of bismuth from the lead is a matter of special importance. Refining processes resolve themselves into the separation of copper by liquation or by means of zinc, and the extraction of other metals, with the exception of bismuth and the precious metals, by melting in an oxidising atmosphere.

If the amount of copper is considerable, the lead is first liquated in a special liquation furnace; otherwise the copper, together with some other constituents, is eliminated when the lead is melted in the desilverising pots or in the refining furnace, in the form of a scum, which rises to the surface of the molten metal and can be skimmed off, further purification of the lead being effected by prolonged oxidation.

In the desilverising of lead by means of zinc, a very perfect separation of copper is effected, as the last portions alloy with the zinc and are taken off with the zinc scum.

The oxidising fusion is effected by the agency of air, or when certain elements are present, steam or lead oxide may also be used as oxidising agents.

Iron, which is only present to a small extent in lead (0·02 to 0·07 per cent.), is easily oxidised as soon as the temperature of the molten bath of metal reaches dull redness; sulphur behaves similarly, and also nickel and cobalt if not present in excess.

Zinc easily oxidises when the molten lead attains a red heat in contact with air, or it is also readily attacked and removed as oxide by blowing steam through the molten metal, hydrogen being liberated at the same time. It can also be removed by melting with litharge in reverberatory furnaces, or, as was formerly practised, by smelting the zinciferous lead with tap cinder in blast furnaces, the zinc going into the slag. Zinc can also be removed as chloride by melting the lead with chlorides such as common salt or *Abraumsalz*. As a rule, air is employed as an oxidising agent for the removal of the zinc, or, to a lesser extent steam, the use of chlorides being rare.

Arsenic and antimony, when present in lead, are oxidised at a cherry red heat in presence of air, forming arseniate and antimoniate of lead which separate out as dross on the surface of the molten metal. The oxidation of both metals is promoted by a blast of air and by making lead oxide serve as an oxidising agent, the use of an air-blast being particularly necessary when large quantities of arsenic and antimony are present. The separation of the foreign metals is promoted by constantly renewing the surface of the lead exposed to the

oxidising agent, and to attain the same end steam is blown through the lead or it is poled with green wood, the violent agitation produced in both cases exposing large surfaces of fresh lead to the air. Saltpetre and sodium carbonate and hydrate were formerly also used as oxidising agents.

Lastly, argentiferous lead may be purified by electrolysis (Keith's process), but for economical reasons this method has not come into general use.

The selection of the particular form of apparatus to be used for the purification of lead, depends upon the degree of purity required, the forms of apparatus being fore-hearths, pots of cast-iron or cast-steel and reverberatory furnaces.

Purification in the fore-hearth is only resorted to when the amount of impurity present in the lead is small, consisting chiefly of small quantities of copper or zinc; antimony when present in small quantities can also be removed by poling the metal at a red heat.

Purification is carried on in pots with varieties of lead which do not contain too much copper, and a proportionately small quantity of antimony and particularly of arsenic; zinc, however, may be present up to the point of saturation.

The refining in reverberatory furnaces is applicable to all varieties of lead containing larger amounts of copper, arsenic and antimony, and reverberatory furnaces are also used for extracting the zinc from lead which has been desilvered by its means. If very large percentages of copper are present, a preliminary liquation is resorted to before refining, but otherwise the elimination of the copper is effected in the reverberatory, refining or softening furnace, before the other impurities present are removed.

Refining in fore-hearths

When molten lead at a red heat is permitted to cool down in order that it may attain the necessary temperature for casting into moulds, the copper and zinc contained in it separate out on the surface as a skin or crust (*krätze*, *bleidreck* or *schlicker*), and this skin is removed by means of a wooden or iron scraper as fast as it is formed. Large quantities of copper cannot, however, be removed in this manner, as the lead soon cools down to the casting temperature.

Small quantities of antimony and arsenic can be removed from lead by poling it with green wood or a bundle of green twigs, when heated to redness in the tapping hearth.

Refining in pots

serves equally well for the separation of copper, nickel and cobalt as for other elements, the copper or nickel and cobalt separating out on the surface of the bath of metal when it is first melted. The last portions of copper can be removed by the addition of zinc, which alloys with the copper, and the alloy rising to the surface can be skimmed off.

For the removal of the other elements (tin, arsenic, antimony and zinc), the bath of metal must be heated to redness and exposed to the action of the air as much as possible, poling or the blowing through of steam being employed for this purpose. When steam is blown through, the pot is covered with a hood having an exit pipe for the vapours and an opening for the entrance of air. If the molten bath contains zinc, the water is decomposed, hydrogen being evolved, so that the presence of air is not requisite in this case; antimony and arsenic, however, exert no such action, and the presence of air is therefore necessary in case they exist in the lead.

Pots are chiefly used for refining when the desilverising and refining processes are worked in conjunction.

In desilverising lead by the Pattinson process (*see* Silver) high temperatures are not used. The process depends upon the fact that if molten argentiferous lead is cooled, crystals poor in silver separate out when it attains a certain temperature, whilst the portion still remaining fluid, the mother liquor, is much richer in silver. By several repetitions of this process lead almost free from silver, and a highly argentiferous lead, are obtained. During the frequent meltings, which are effected in cast-iron vessels, the greater portion of the copper, as well as of the nickel and cobalt, separates as scum. Bismuth goes with the silver and collects in the argentiferous lead, but the other elements present are mostly found remaining in the desilverised lead at the end of the operation, as the red heat necessary for their oxidation is not attained in the process. If these elements are present in large quantities, the Pattinson process must be preceded by a refining operation, and if large quantities of copper are present, by liquation also.

The following analyses by Hampe,[1] which refer to lead to be desilverised by zinc, show how completely the Upper Harz lead is purified by a single melting in pots at low temperatures, the metal never being brought to redness. This lead is sufficiently pure to

[1] *Zeitschrift für Berg-, Hütten-und Salinenwesen in Preussen*, XVIII., p. 203.

permit of the preliminary refining before desilverising to be dispensed with:—

	Clausthal.		Lautenthal.	
	Before skimming off the *Abzug*.	After separation of the *Abzug*.	Before skimming off the *Abzug*.	After separation of the *Abzug*.
Lead	98·9294	99·0239	98·9647	99·1883
Copper	0·1862	0·1096	0·2838	0·0907
Bismuth	0·0048	0·005	0·0082	0·0083
Silver	0·1412	0·142	0·1413	0·1440
Arsenic	0·0064	0·0053	0·0074	0·0032
Antimony	0·7203	0·7066	0·5743	0·5554
Iron	0·0064	0·0042	0·0089	0·0048
Zinc	0·0028	0·0017	0·0024	0·0015
Nickel	0·0023	0·0017	0·0068	0·0038
Cobalt	0·00016	traces	0·00035	traces

For the zinc desilverising process the lead must only contain a small amount of copper, otherwise the zinc added is taken up by the copper, consequently cupriferous leads require to be liquated before desilverising. Other elements, too, especially arsenic and antimony may only be present in small amounts, previous refining being necessary if they exceed a certain percentage.

The zinc desilverising process depends upon the fact that if zinc be melted together with argentiferous lead and the whole allowed to cool, the silver alloys with the zinc and collects as a scum or crust upon the surface of the molten mass. The lead takes up about 0·5 per cent. of zinc which it retains after the desilverising.

As zinc possesses even a greater affinity for copper than it does for silver, the process of desilverising by zinc effects a very complete removal of any copper contained in the lead. The other metals which are present, especially antimony and arsenic, chiefly remain behind in the lead, and are separated together with the zinc absorbed during desilverising, by refining. This refining is effected by heating the metal to a cherry red heat and passing steam through it, air being excluded at first, and after the zinc has been eliminated in that way, the remaining elements, particularly antimony and arsenic, are got rid of by continuing the current of steam and at the same time permitting the air to have access to the bath of molten metal. The zinc is eliminated either as a powdery dross or as a fluid scum, antimony forming a fluid *abstrich* solidifying to a black or grayish-black mass, or the zinc and antimony may be both contained in the same scum.

It is possible to eliminate zinc by blowing air through the molten

mass, but the oxidation of the lead is excessive. Attempts have also been made to eliminate zinc alone by blowing carbon dioxide through the molten mass kept at a red heat; though this has proved to be a success in experiments conducted on the small scale, it has not answered in practice where gases containing only 15 to 20 per cent. of carbon dioxide have been employed.

The removal of zinc as chloride by treating the metallic bath with sodium chloride or *Abraumsalz* is only at present very rarely used.

Refining in pots is a quick process, a pot full of lead holding from 12·5 to 20 tons requiring only from three quarters of an hour to three

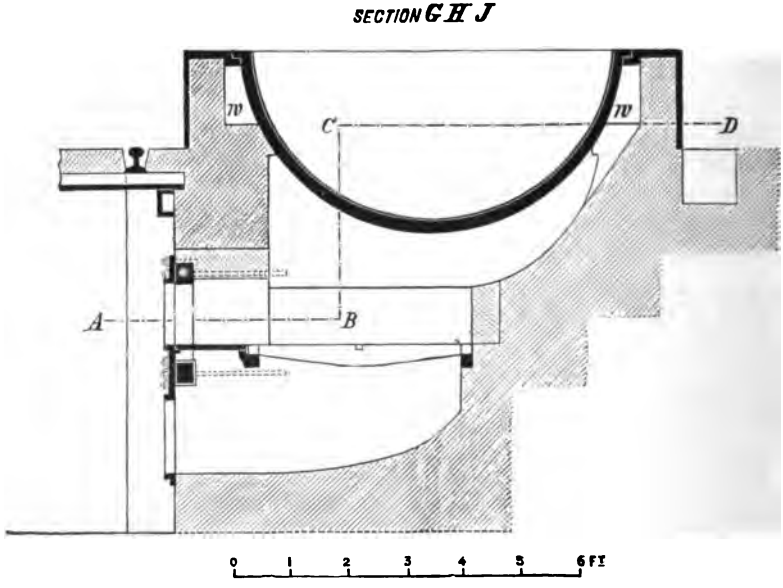


FIG. 273.

hours; as, however, it is necessary to heat the vessel to redness it entails a considerable outlay both for pots and for fuel, and more oxide and scums are produced than when refining in reverberatory furnaces. The pots are especially attacked at the edge of the layer of molten metal when arsenic is present, and large amounts of antimony hasten the corrosion of the vessel. Against this must be set the smaller loss of lead when refined in pots as compared with the loss in reverberatory furnaces.

The refined lead was formerly removed from the vessel by ladles,

but at present it is most conveniently syphoned off or else pumped out by means of a Rösing's lead pump.

The arrangement of a pot for a 15-ton charge is shown in Figs.

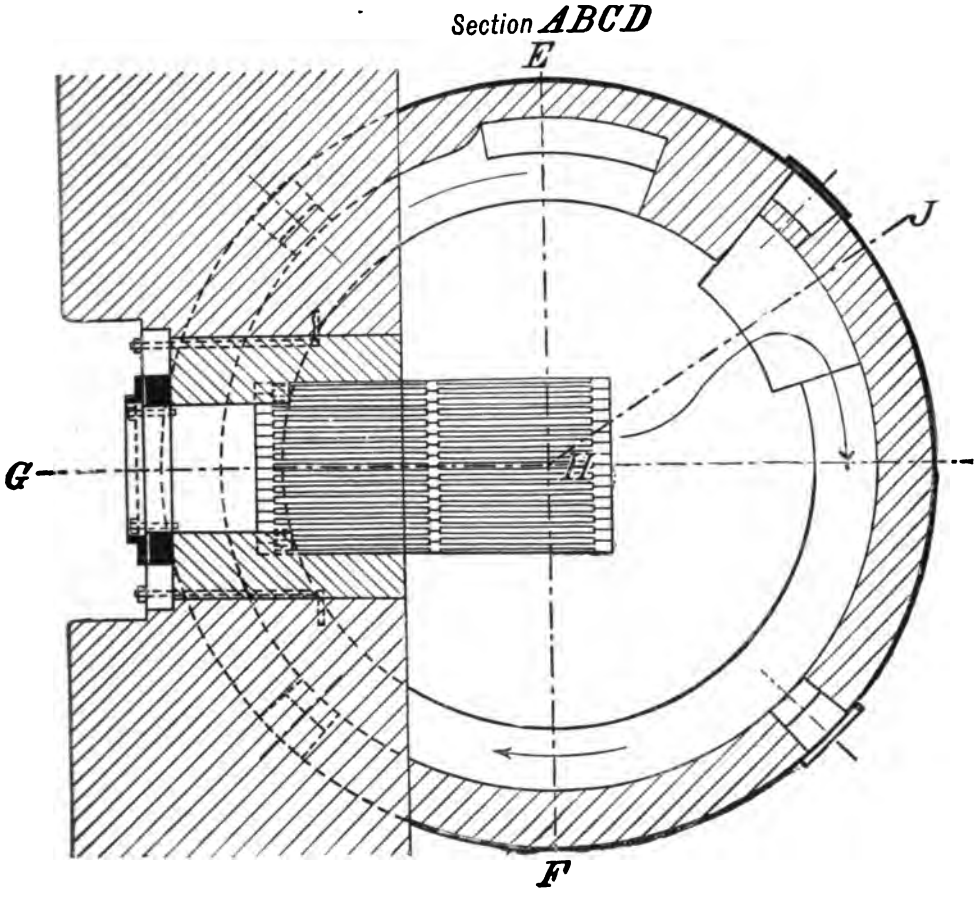


FIG. 274.

273 to 276. The hot gases from the fire come in contact first with the bottom of the vessel, then pass through an opening in the masonry into a flue running round the upper part of the pot, and after circulating round the vessel pass away by *y* to the flue *z* leading to the stack.

The arrangement for passing steam into the mass is shown

in Figs. 278 and 279. The cast-iron pipe z is bolted to the branch m of the steam-pipe d; m can be closed by a blank flange when steam is not required.

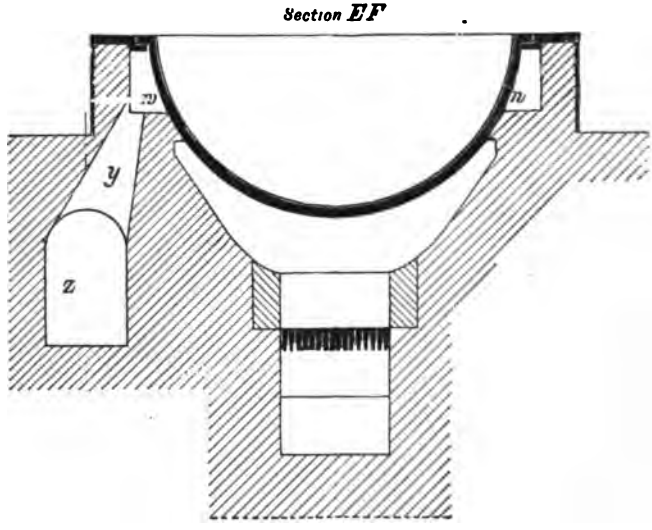


FIG. 275

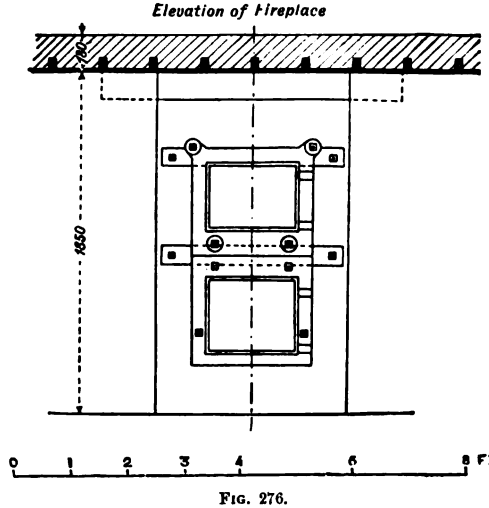


FIG. 276.

The process in use in the Upper Harz may be taken as an instance of the combined desilverising and refining process conducted

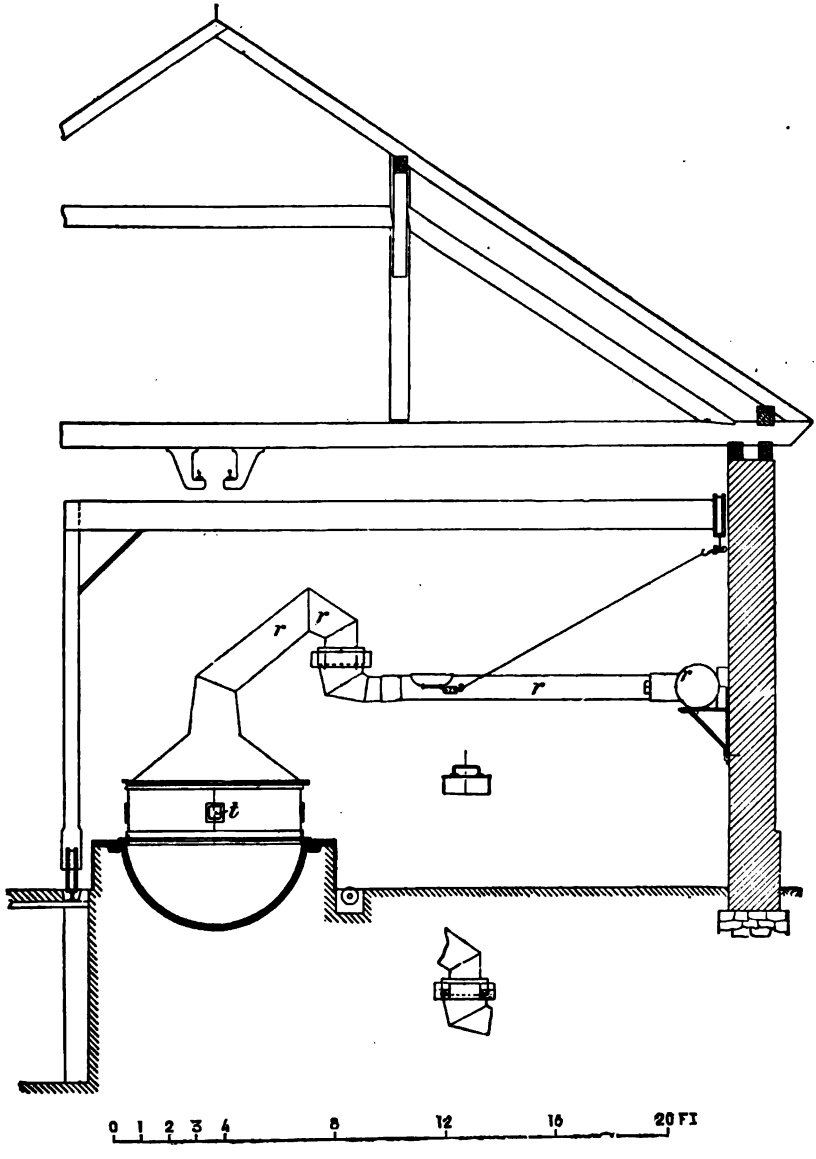


Fig. 277.

in pots. The lead which is treated there has (according to Hampe) the following composition :—

	Clausthal.	Lautenthal.	Altenau.
Lead	98·2944	98·9647	98·8378
Copper	0·1862	0·2838	0·2399
Antimony	0·7203	0·5743	0·7685
Arsenic	0·0064	0·0074	0·0009
Bismuth	0·0048	0·0082	0·0039
Silver	0·1412	0·1421	0·1400
Iron	0·0064	0·0089	0·0035
Zinc	0·0028	0·0024	0·0025
Nickel	0·0023	0·0068	0·0028
Cobalt	0·0001	0·0003	0·0001

The lead is melted in cast-iron pots holding 12½ tons, 6 hours being required. During this period the greater part of the copper separates out as a crust (*schlicker*) on the surface of the bath,

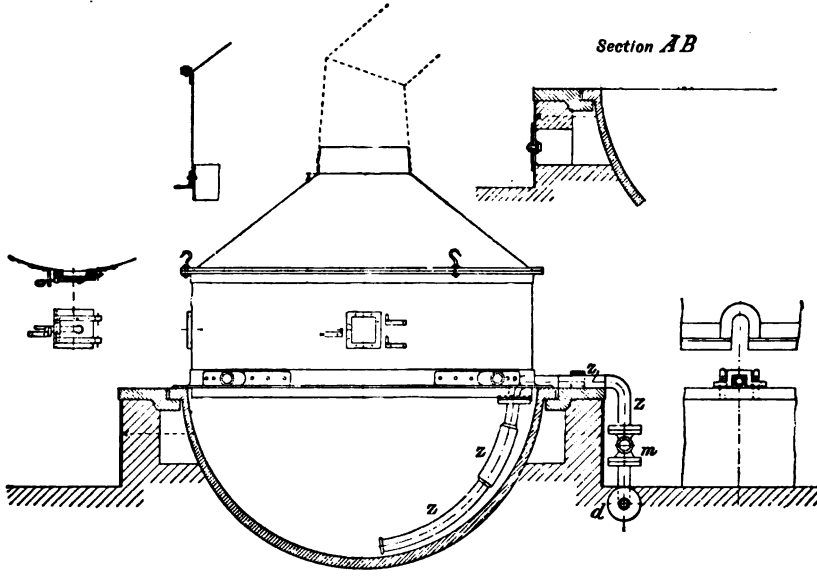


FIG. 278.

and this is skimmed off. The silver is next extracted from the lead by means of zinc (*see* Silver), this requiring 15 hours, the zinc also extracting the copper very completely as shown by the analyses which follow. After desilverising, the lead will have taken up 0·7 per cent. of zinc and still retains the greater part of the antimony.

The separation of these bodies is at once proceeded with in the same vessel, the zinc being first eliminated by blowing steam through in the absence of air, and then the antimony by the combined action of steam and air. With this object the bath of molten metal, which is at a low temperature at the conclusion of the desilverising operation, is heated strongly for 4 hours, the temperature reaching dull redness; the hood before mentioned is then placed over the pot in order to exclude air, and steam at $2\frac{1}{2}$ atmospheres pressure is led in by the cast-iron pipe to the bottom of the pot; hydrogen is evolved and zinc oxide rises to the surface. It is not possible to completely

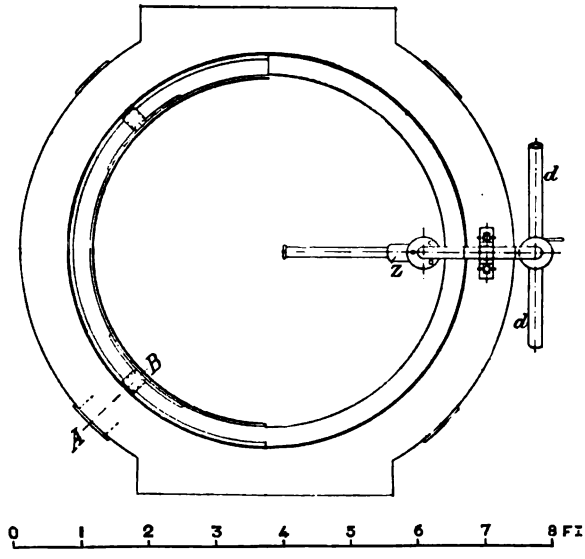


Fig. 279.

exclude air; some is introduced with the steam, some finds its way in through imperfect fitting of the hood and through the wide draught pipe, and consequently a portion of the lead and antimony is also oxidised in addition to the zinc. Samples taken at intervals gave, according to Kuhlemann, 0·40 per cent. of zinc after passing steam through for half an hour, 0·116 per cent. after an hour and a half when only a little "zinc rag" still formed on pouring from a ladle, and 0·0004 per cent. of zinc when no more "rag" was produced and the oxides appeared perfectly dry. This shows that the elimination of the zinc is complete, 2 hours being as a rule required. After removing the hood, the yellow powder on the surface of the bath, consisting of a mixture of zinc and lead oxides and small shots of

lead, is taken off with a ladle, the hood is replaced, the four doors in it opened, and steam again passed through. The air drawn through the doors of the hood now oxidises the antimony, which collects as a blackish fluid mass on the surface of the molten metal; this scum known as *abstrich* is a mixture of lead and antimony antimoniates. The process lasts about two hours, and its termination is marked by the formation of ordinary yellow litharge, the lead remaining after the *abstrich* is removed being pure. The contents of the pot are now allowed to stand for about an hour to cool down, and are then drawn off with the aid of a lead pump and cast into moulds. Each pot lasts some 20 or 30 charges, or if the amount of antimony present is small it may serve for 40 or 50 operations.

The composition of the refined lead is shown by the following analyses made in the Royal Laboratory at Clausthal:—

Analyst.	Fraatz.	Fraatz.	Rösing.
Bismuth	0·00737	0·004437	0·00858
Copper	0·00072	0·00061	0·00028
Antimony	0·00441	0·00406	0·00497
Silver	0·0006	0·0005	0·00030
Cadmium	traces	traces	0·00082
Iron	0·00116	0·00096	0 00082
Nickel	traces	traces	0·00126
Zinc	0·0005	0·00030	0·00086
Lead	99·98524	99·9892	99·98275

Before the introduction of the zinc desilverising process the market lead of the Upper Harz was obtained by Pattinson's process, and this lead was less pure than that obtained by the zinc method as shown by the following analysis:—

	Altenau Streng).	Clausthal (Hampe).	Lautenthal (Hampe).
Copper	0·02	0·039	0·0374
Antimony	0·04	0·004	0·0016
Iron	0·0035	0·004	0·0044
Zinc	0·008	—	—

The content of silver in the above samples was 0·0025 per cent. At Hoboken, near Antwerp, Spanish lead from Mazarron is desilverised by zinc and purified by steam at a pressure of 5 atmospheres, the zinc and antimony being both collected together in the same *abstrich*.

Refining of lead in reverberatory furnaces

This is the cheapest method of softening lead, and is particularly applicable when large quantities of arsenic and antimony are present.

If much copper is present the lead as previously mentioned is first submitted to a process of liquation in a special furnace (*saiger-flammofen*). The furnace is built with a sloping hearth made of

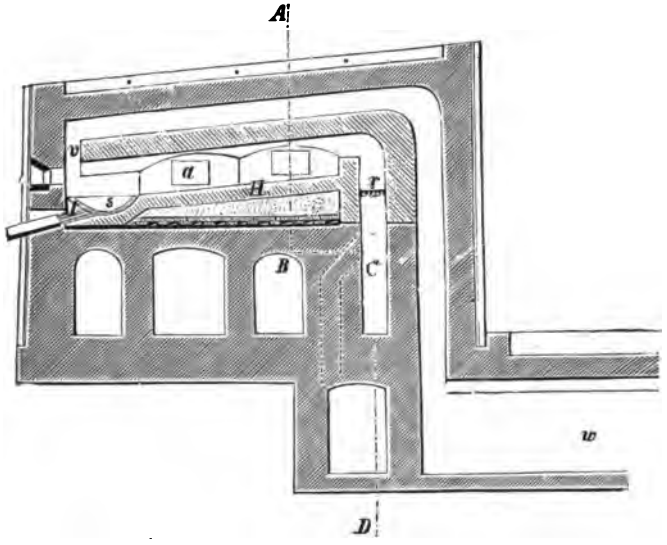


FIG. 280.

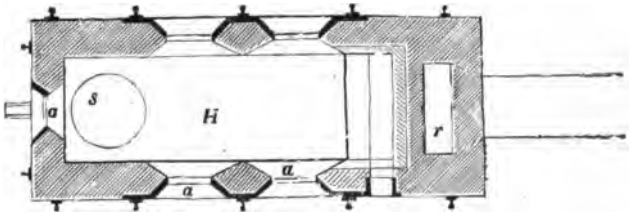


FIG. 281.

loam, brasque or fireclay, and the liquated lead is either collected in a sump at the lower end and periodically tapped out from it, or else it continually drains away from the furnace into a heated pot placed to receive it.

The Freiberg and Przibram furnaces are provided with sumps inside the furnace, the arrangement at Przibram being shown in Figs. 280 to 282.

The hearth H is made of marl, and slopes down to a sump s beaten out of brasque from which the lead is tapped at intervals by the tap hole t. The cupriferous work-lead which is to be liquated is put on to the hearth through the working doors a, a; the lead liquates out and flows down into the sump, whilst the copper, nickel and cobalt, together with a portion of the lead, remain behind as a solid mass (*saigerdörner* or *saigerkrätzen*) which is raked out of the furnace through the doors a, a; r is the grate, v the flue and w the flue leading to the stack.

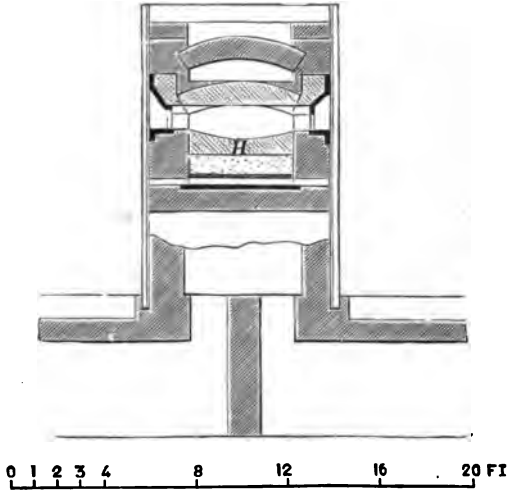


FIG. 282.

The Freiberg liquation furnace is shown in Figs. 283 and 284, and is worked with an air-blast below the firegrate. H is the hearth, r the grate, v the pipe supplying the air, s the sump, z the flue leading to the stack w; m, m are working doors, and u is a cast-iron spout for running off the lead from the sump.

The Freiberg lead, which is liquated before being desilverised by Pattinson's process, has the following composition according to Schertel:—[1]

Silver	0·544	Nickel } Cobalt }	0·055
Copper	0·94	Iron	0·027
Bismuth	0·066	Zinc	0·022
Arsenic	0·449	Sulphur	0·200
Antimony	0·82		
Tin	0·210		

Twelve tons of lead are liquated in 12 hours with a consumption of 14 cubic feet of inferior coal. The liquation residue forms 2 to 5

[1] *Jahrbuch für das Berg-und Hüttenwesen im Konigreich Sachsen*, 1882.

per cent. of the weight of the lead used, and contains 96 per cent. of the nickel content of the original lead, 93 per cent. of the copper and

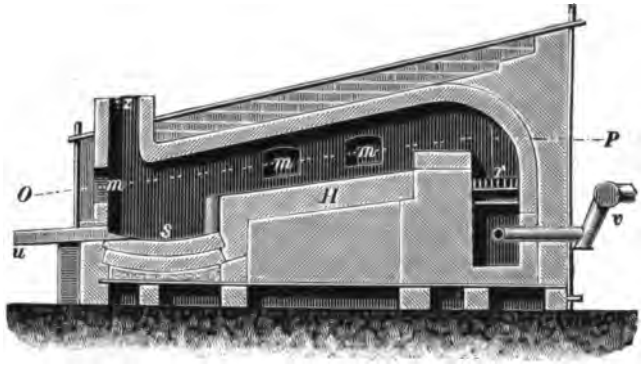


FIG. 283.

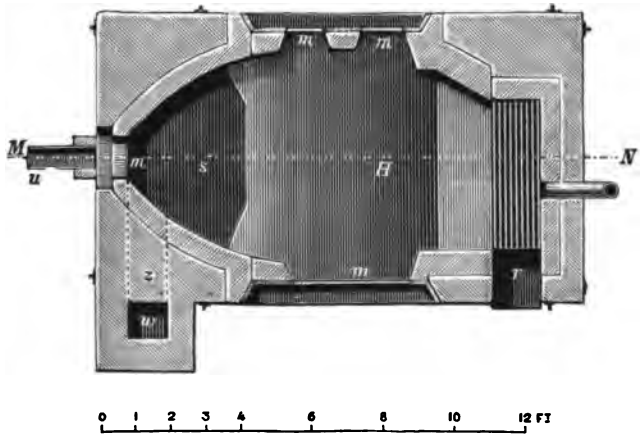


FIG. 284.

25 per cent. of the arsenic; it has according to Schertel the following composition :—

Silver	0·17	Antimony	0·98
Lead	62·40	Tin	0·04
Copper	17·97	Nickel \ Cobalt /	1·09
Arsenic	2·32		

In the furnace described as in use at Przibram, 13 tons of lead containing 0·07 to 0·1 per cent. of copper are liquated in 24 hours, yielding about 6 per cent. of liquation residue containing 80 to 90 per cent. of the copper of the original lead.

The reverberatory *improving* furnace is used both for the elimination of the copper contained in the lead and of the other impurities

as well by an oxidising fusion. Where rapid working is the rule, as in the desilverising works of the United States, the copper is found in the scums taken off in the refining furnace, and these scums are liquated alone in a special furnace, yielding a considerable amount of argentiferous lead and a residue rich in copper. The lead is desilverised, and the cupriferous residue is smelted together with galena, yielding copper-lead matte, which is further worked up for copper, silver and lead. The reverberatory furnace is worked with natural draught, and if the lead is very impure a blast of air is directed over the molten surface. The older furnaces held 10 to 20 tons, the later ones hold 30 to 35 tons or in rare cases in some works in the United States as much as 50 tons. The hearths are elliptical or rectangular, the length being from one and a half times to twice the width, and the depth varying from 11 to 16 inches, and occasionally reaching as much as 21½ inches. In England, deeper furnaces, holding over 100 tons, are in use.

In modern furnaces the hearth is built on a shallow iron pan in order to avoid loss of metal; these pans were at first constructed of cast-iron, but on account of their great tendency to crack they have been generally replaced by wrought-iron. The hearth bottom is made of marl or firebrick, and as it is soon eaten away by the lead and antimony oxides, it is built in two layers of firebrick. Either the entire hearth or the side walls only are surrounded with a water jacket in order to diminish as far as possible the action of the oxides upon the material composing the hearth. In the first case the iron pan on which the hearth is built is surrounded by a second wrought-iron pan, and the cooling water circulates in the space between the two, which is from 3 to 4 inches wide. In the most recent pans the sides only are water-jacketed, the cooling of the bottom being considered superfluous.

Figs. 285 to 288 show the details of the older furnace without any cooling arrangement, in use at Przibram in Bohemia. The hearth is of marl, the furnace holds 22 tons and is provided with an air-blast; *h* is the hearth, *m* the heating chamber, *r* the grate, *f* the flue; *a*, *a* are the blast pipes one on each side of the hearth, *n* the hollow air-cooled fire bridge; *g*, *g* are working doors, *w* is the tap hole through which the refined lead is run out of the furnace.

A modern American furnace with wrought-iron pan, the sides of which are water-jacketed, is shown in Figs. 289 to 293; *a* is the fireplace, *c* the pan made of boiler plate ⅜ inch thick which encloses the hearth up to the working doors (3 feet 6 inches high), *b* is the water jacket also made of ⅜ inch thick boiler plate. It is 3 inches

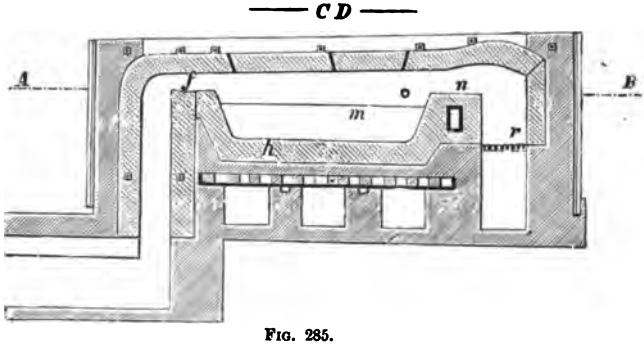


FIG. 285.

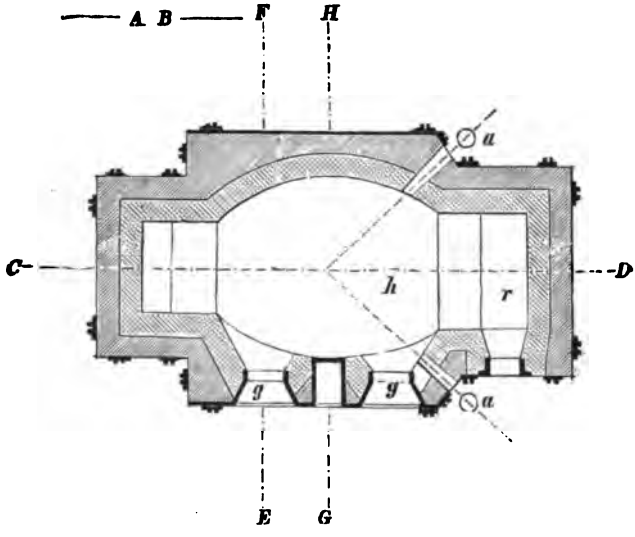
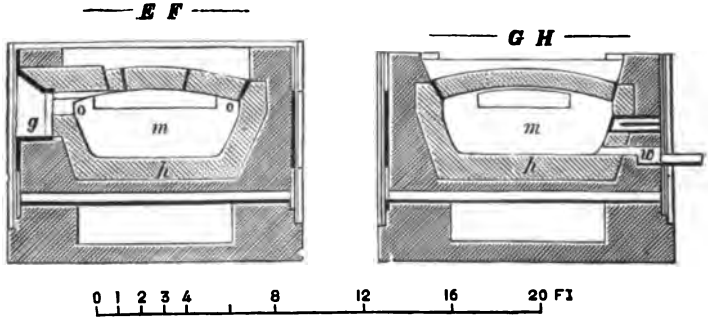


FIG. 286.



FIGS. 287 and 288.

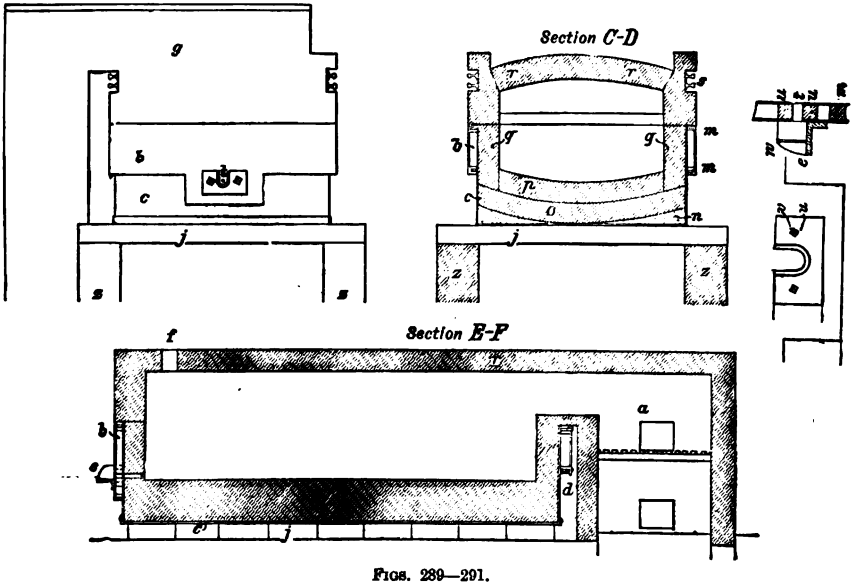
wide inside and 1 foot 9 inches high, and is supplied with water through a pipe 1¼ inches diameter, the water flowing away through another pipe of the same size; the hearth is 16 feet long and 8 feet broad, including the water jacket; *d* is the hollow air-cooled fire bridge, *f* is the flue leading into *g* and thence to the stack. In one of the longer sides of the furnace there are three working doors *i*, and only two, *h*, on the opposite side; through the latter the lead is charged in to the furnace, whilst the scums and dross are withdrawn through the former. The doors *i* are let into the water jacket for a depth of 3 inches, but *h*, *h* are level with the upper edge of the jacket. The pan rests on iron bearers, *j*, *j*, of I section, they in turn resting on the masonry *z*. On the bottom of the pan is a layer of brickdust, and on that two layers of firebrick *o* and *p*; the lower layer is of less refractory brick and the upper of the best quality of fireclay, the bricks being set as closely as possible in fireclay mortar. The side walls of the furnace, *q*, are constructed of firebrick, which reaches down to the lower layer *o* of the firebrick of the hearth, and the corrosion of the hearth is confined to the upper layer *p* of the hearth and to a certain depth of the side walls *q*. The hearth slopes to the tap hole *t*, which consists of a conical iron tube passing through the water jacket and ending in the cast-iron spout *e*. The tap hole is closed either by clay rammed into it or by an iron rod tipped with clay.

In the refining process the lead is first melted on the hearth, and any scum which rises is taken off; the temperature is then raised to dull redness, and if an air-blast is employed this is now brought into action. Tin is the first impurity to oxidise and is removed as a dross, then the oxidation of the antimony, arsenic, and other easily oxidisable elements follows.

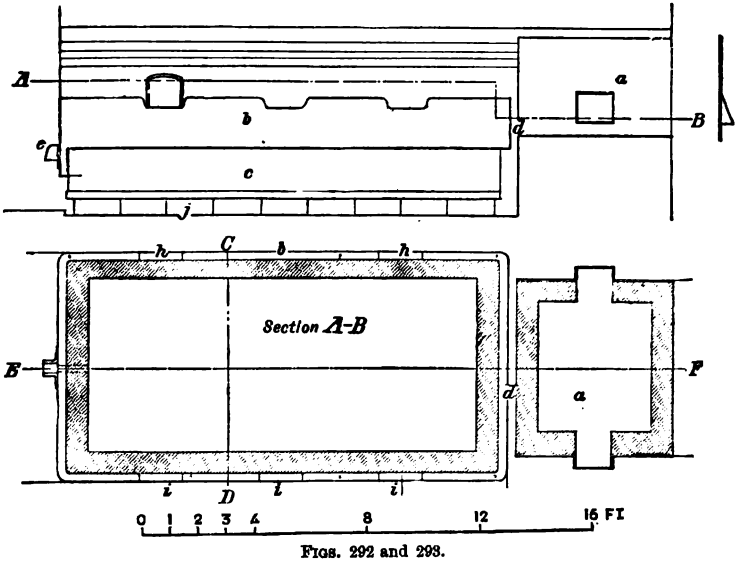
As antimony is only slowly oxidised under these circumstances, its removal is facilitated in many works by the addition of litharge, or just as in the refining in iron pots, steam is passed through the molten bath by means of an iron pipe. By this means the time required for the oxidation is reduced by one half, but large quantities of oxide are formed which collect at the side of the furnace and rapidly corrode the side walls, so that the process is only employed when actually necessary.

The antimony scum (*abstrich*) is allowed to cool somewhat so as to enable it to be drawn out as a solid crust, the doors of the furnace being opened for this purpose. In the case of lead poor in antimony one such operation is sufficient, otherwise it is repeated several times, the refining being finished when nothing but litharge forms on the surface of the molten metal. The bath is then cooled

by leaving the doors open, and the still molten lead is tapped out and run into moulds, either by means of a syphon or a spout moving in



FIGS. 289—291.



FIGS. 292 and 293.

a semicircle and delivering the lead into the empty moulds also arranged in that form.

The amount of the scums produced depends upon the percentage of foreign matters in the lead, the first scum (*schlicker*) being on an average 4 per cent. of the weight of the original lead, whilst the second scum (*abstrich*) amounts to about 5 per cent. In modern furnaces 156 lbs. of coal are used for every ton of lead refined.

The form of furnace just described is employed for refining lead which is to be desilverised, lead which has been desilverised or lead free from silver. In the purification of lead desilverised by means of zinc 4 to 5 per cent. of zinciferous scum containing 90 per cent. of lead is produced, and a charge of 30 tons is purified in 14 hours, 1 cwt. of coal being used for each ton of the original lead.

In the Przibram furnace before described, 22 tons of liquated lead are refined in 24 to 26 hours, the consumption of fuel being 9 per cent. of the weight of the lead, and 81 per cent. of refined lead being obtained, having, at Przibram,[1] the following composition :—

	1	2	3	4
Silver	0·00015	0·0014	0·0017	0·0013
Copper	0·0009	0·0021	0·00119	0·0012
Bismuth	0·0022	0·0018	0·00185	0·0021
Iron	0·001	0·001	0·0011	0·0017
Antimony	0·0016	0·0029	0·0032	0·0029
Zinc	traces	0·0008	0·0012	0·0011

At Freiberg the refining of argentiferous lead before pattinsonising is effected after previous liquation in a furnace similar to that used at Przibram, an air-blast being employed. The lead is introduced in several charges, the first of 6 tons, and after this is melted a second of 10 tons and then a third charge of 5 tons. The first scums are rich in tin and arsenic which are smelted as before mentioned for tin-lead, and then arsenical and antimonial *abstrich* follow, which are smelted for hard lead. The refining of 21 tons may take as long as 36 hours, the time depending upon the percentage of impurity present. In an operation lasting that time, 24½ cubic feet of lignite and 10½ cubic feet of coal are used, 85 per cent. of refined lead containing 0·5 to 0·7 per cent. of silver being obtained.

At Port Pirie in South Australia the argentiferous lead from Broken Hill is refined, without previous liquation, before being desilverised. Figs. 294 to 298 show the construction of the furnace used which has a water-cooled fireclay hearth. The charge consists of 22 tons of lead with 250 to 350 ounces of silver per ton, and this

[1] *Oesterr. Zeitschr.* 1885, p. 208.

is refined in 14 to 16 hours, 1·5 tons of coal being used. One man is required to work the furnace during the shift, being assisted by two labourers in the charging operation, which lasts 1½ hours. The total amount of scums reaches 2½ to 3 tons from the 22 ton charge; the first scum is cupriferous and is smelted in blast furnaces with galena for copper matte. The second, third, and fourth scums are rich in antimony, and are liquated and then smelted for hard lead.

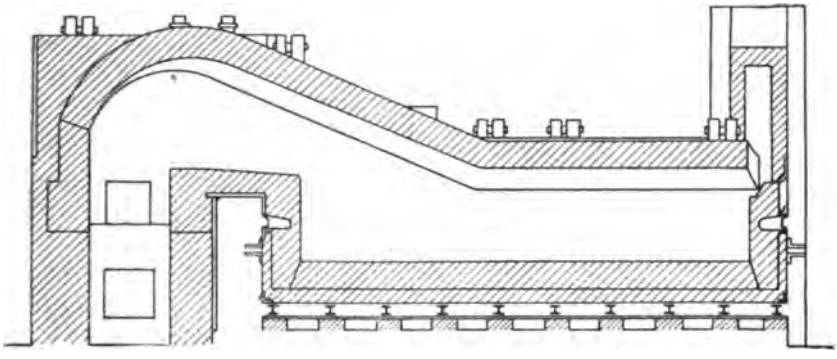


Fig 294.

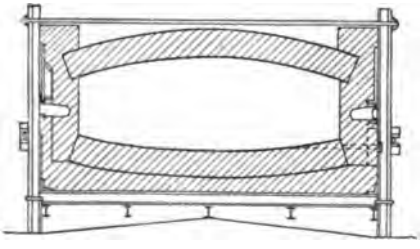


Fig. 295.

At Cheltenham near St. Louis (Missouri) 38 to 40 tons of lead are refined without previous liquation in from 15 to 30 hours, according to the degree of impurity of the lead. The consumption of coal varies, according to the duration of the work, from 1¼ to 2½ tons, and the labour required is 1½ men per furnace per 12 hour-shift.

After desilverising by zinc, the lead is freed from the zinc taken up, by a refining in the same furnace. A quantity of 36 tons is treated at one time, the refining lasting 12 to 18 hours, and the coal consumption averaging 2·2 tons, including the coal used in heating the casting pot, the labour requirements being the same as in the last instance.

At the works of the Omaha and Grant Smelting and Refining Company at Omaha in Nebraska, large refining furnaces holding 45

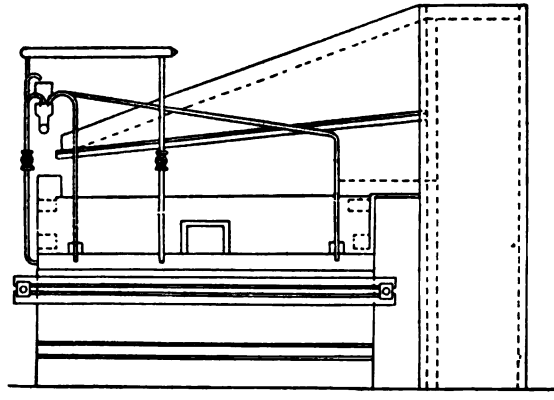


FIG. 296.

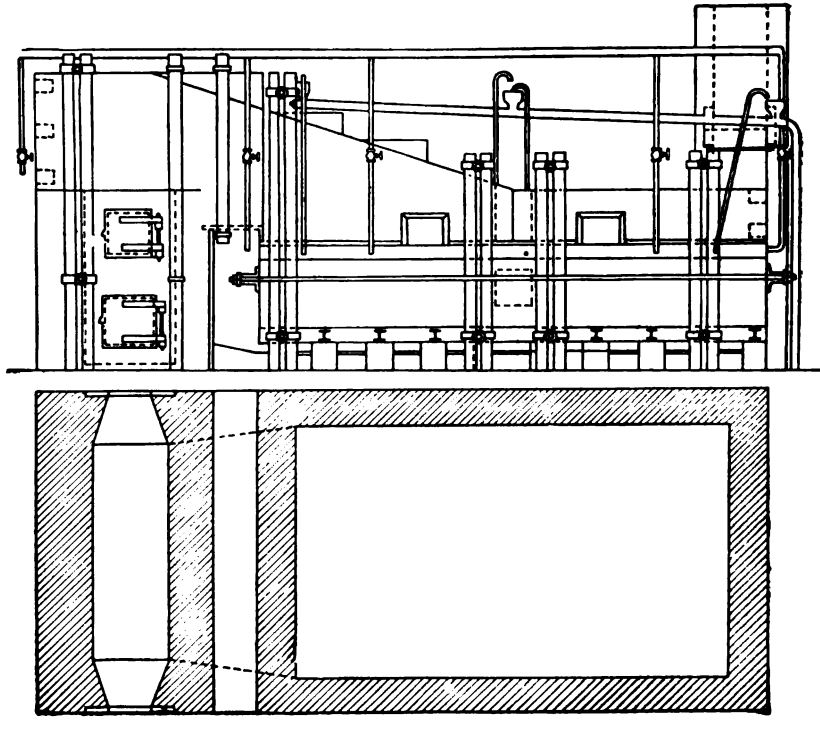


FIG. 297 and 298.

tons of lead are in use, in which lead carrying 300 ounces of silver per ton is refined before being desilverised by means of zinc. The

refining of this amount takes 12 hours, and 1½ tons of coal are used. Scums are obtained, which are smelted together with galena for copper matte, and work-lead, and antimonial dross, the latter being smelted for hard lead after liquation.

At the National Works near Chicago (Illinois) the refining furnace is heated with the fluid residues remaining after the distillation of crude petroleum. The charge consists of 37 tons of argentiferous lead containing 2 to 3 per cent. of antimony, and litharge is added to the bath to hasten the oxidation of the antimony. The whole operation lasts 12 hours, and 32 to 35 tons of refined lead are obtained. The cupriferous dross is smelted with galena in reverberatory furnaces, litharge and cupriferous lead matte being produced; the latter is treated with an air-blast in a refining furnace, giving lead slags and a concentrated copper matte which again undergoes the same operation. The final products are lead slag and coarse copper, containing both gold and silver, the so-called copper bottoms. The antimonial dross is liquated and then smelted for hard lead.

The casting of refined lead

The lead after refining has to be cast into moulds. It is allowed to cool until it attains the requisite temperature, and the usual practice in former days was to then ladle it out of the furnace or refining pot into the moulds. Ladling is seldom resorted to at the present day, and it is usually run through a tap hole into a launder or a pipe movable in a semicircle, and thence into a series of moulds arranged in a semicircle, or else it is run out into heated pots and syphoned or pumped over into the moulds. The use of the syphon is preferable, or if the levels of the vessels will not allow of this, then Rösing's lead pump may be used.

The arrangement used in works in the United States is shown in Fig. 299.[1] A tube 2 inches in diameter provided with a stopcock *c*, passes through the tap hole and is connected with the pipe *g*, 6 to 10 feet long, by means of the vertical pipe *e* and the swivel elbow *f*, this allowing of the pipe being turned horizontally in a semicircle by means of the handle *h*; when the lead is ready to tap, the cock *c* is heated by fire applied to it, and opened, when the lead flows out through the pipe into the moulds placed to receive it. The pipe *g* is usually previously warmed before screwing it into the elbow *f* by dipping it into the bath of lead in the furnace, and after fixing it in position the cock

[1] Hofman, *op. cit.*

c is opened fully so as to prevent the lead solidifying in the tube; it is then half closed so as to moderate the violence of the flow.

This method of tapping has the drawback of necessitating the cooling of the refining furnace down to the casting point, which takes some time and necessarily diminishes its output, so that the better plan is to run off the lead into a hot iron pot and syphon into moulds from the latter.

A syphon arrangement, contrived by Steitz and in use at some of the American desilverising works, for running the desilverised lead into the refining furnace, is shown in Fig. 300. The syphon is of

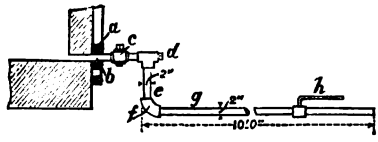


FIG. 299.

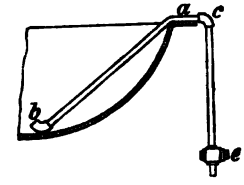


FIG. 300.

bent gas tubing 2 to 2½ inches wide, one end of which reaches to the bottom of the pot, the other being connected by an elbow *c* with a vertical pipe provided with a cast-iron stopcock *e* at its lower end. The end of the tube dipping into the pot is furnished with an elbow *b* resting on the bottom of the pot. The lead discharged from the cock flows into a launder of cast-iron and from that into the refining furnace.

If it is desired to cast the lead directly into the moulds, the vertical portion of the syphon is connected with a pipe movable horizontally in a semicircle, from which the molten lead runs into the moulds.

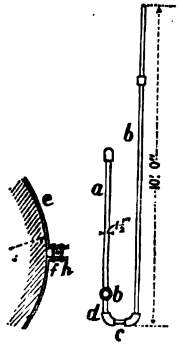
A similar arrangement is shown in Figs. 301 and 302,[1] where *i* is the longer limb of the syphon outside the pot, and *j* is a cast-iron stopcock on it. It is connected to a movable joint into which the tube *p*, which is 10 feet long, is screwed. This can be turned round in a half circle by the handle *q*, the movable portion *m* being furnished with a pivot resting in the socket *o* (Fig. 302).

Rösing's lead pump is only used when the position of the containing vessel renders the use of a syphon impracticable as, for instance, when the pot is on the ground level. The pump lifts the lead by means of direct steam pressure and acts very satisfactorily.

The moulds in which the lead is cast vary in form according to the requirements of the trade. A shape common in the United

[1] Hofman, *op. cit.*

States is shown in Figs. 303 to 305, this having been found convenient for quick casting.[1] One end is furnished with wheels, the



Figs. 301.

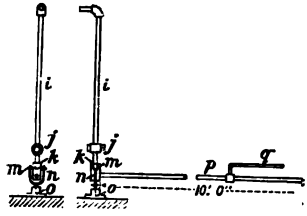


Fig. 302.

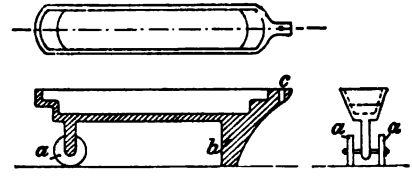


Fig. 303—305.

other rests on the bearer *b*, a handle can be hooked through the hole *c*, the mould and contents wheeled away, and the ingot tipped out, and the mould is then again ready for use.

The composition of desilverised and refined American market lead is shown by the following analyses :—

	Pennsylvania Lead Co.	Consolidated Kansas City Smelting and Refining Company.	
	I.[2]	II.[3]	III.[3]
Copper	0·00007	0·00022	traces
Silver	0·00042	0·0002	0·0004
Bismuth	—	0·00308	—
Antimony	0·00051	0·00127	0·0004
Iron	traces	0·00178	0·0006
Zinc	0·00038	0·00075	0·0013
Manganese	—	0·00021	—
Sulphur	0·00018	—	—
Lead	99·99844	99·99249	99·9963

[1] Hofman, *op. cit.*

[2] *Trans. A.I.M.E.*, iii. p. 322.

[3] *Engin. and Min. Journ.*, July 14, 1882.

SILVER

Physical Properties

Silver has a pure white colour and a perfect metallic lustre. It is exceedingly malleable and ductile, being only second to gold in these properties; it is harder than gold, but softer than copper. The specific gravity of silver according to G. Rose lies between 10·514 and 10·619 at 14°C, and according to Matthieson it is 10·468 at 13°C. It crystallises in the regular system.

Its conductivity for heat stands to that of gold in the ratio of 100 : 102·8 (Despretz), 100 : 98 (Calvert and Johnson), 100 : 60 (Wiedemann and Franz). According to Regnault its specific heat is 0·05701 and according to Bunsen 0·0559.

Silver is of all the metals the most perfect conductor of electricity; if its conductivity be taken as 100, that of gold is 73, and of copper 72 to 77 (Matthieson).

It melts at about 1000°C (according to Becquerel at 960°C, and according to Riemsdyck at 1040°C).[1] At high temperatures it volatilises, yielding a green vapour, and it can be distilled by means of the oxy-hydrogen blowpipe.

When in the molten state, it possesses the power of absorbing oxygen from the air to the extent of 22 times its own volume, the gas being given out again on cooling with such vigour that the surface of the silver is thrown up into small bubbles, and particles of the metal are projected. This phenomenon is known as the *spitting* of silver, and only occurs when the silver is pure, small quantities of copper, bismuth or zinc entirely preventing it. The spitting may also be prevented, even with pure silver, by covering the surface with a layer of charcoal powder, common salt, potash or other bodies which possess no oxidising action. The presence of small amounts of arsenic, antimony, bismuth and lead renders silver brittle.

[1] 960·7°C, Heycock and Neville, *Journ. Chem. Soc.* 1895, p. 188.

Chemical Properties.

Silver does not oxidise in either dry or moist air at the ordinary temperature, and only very slightly if the temperature be raised; caustic alkalies, alkaline carbonates, nitre and potassium chlorate are all without action upon it. Nitric acid easily dissolves silver; sulphuric acid only dissolves it when the acid is hot and concentrated. Aqueous hydrochloric acid attacks it only superficially, and vegetable acids are practically without action upon it. It is blackened by sulphuretted hydrogen owing to the formation of silver sulphide.

It combines with chlorine, forming silver chloride, and it is also converted into the same body by the action of certain chlorides such as cupric, ferric and mercuric salts. Gaseous hydrochloric acid passed over heated silver converts it into the chloride, with liberation of hydrogen. Chloride of silver is also formed when finely divided silver is heated with common salt.

Melted together with sulphur, silver is converted into the sulphide.

Silver easily alloys with lead, copper and zinc when melted together with these metals, and forms an amalgam when brought into contact with mercury in the cold, though the amalgamation proceeds much more rapidly when the metals are heated together.

The Chief Chemical Reactions of Silver Compounds that are of importance in its Extraction

Oxides of Silver

The oxides of silver, *viz.* silver oxide (Ag_2O) silver suboxide (Ag_4O) and silver peroxide (Ag_2O_2 or AgO), do not play any important part in the extraction of the metal.

Silver oxide (Ag_2O) is formed in the dry way by heating silver with certain oxides (cupric oxide, red lead, manganese dioxide), with the nitrates or sulphates of lead and copper, or with arsenic acid. Silver oxide is also obtained as a brownish powder by passing a powerful electric discharge through the metal, or by heating the metal in the oxy-hydrogen flame.

Silver when present in litharge is present in part as oxide. As however, according to H. Rose and other authorities, silver oxide is decomposed between 250° and 300°C into silver and oxygen, and as litharge has been subjected for a considerable time to a temperature between 900° and 1000°C, its existence in it might be called in question. In favour of the view that silver exists in litharge as oxide, are the observations of St. Clair-Deville and Debray and those of

Troost and Haute-Feuille[1] that silver oxide can be formed at high temperatures. In addition, Wait has extracted 18·67 and 19·25 per cent. of the silver from litharge containing 2·94 per cent. of silver, by means of acetic acid,[2] and as metallic silver is insoluble in acetic acid it may be assumed that the metal must have been present as oxide. The limiting temperature below which silver oxide is stable must consequently be regarded as not yet definitely settled.

In the wet way silver oxide is obtained as a brownish precipitate by adding caustic potash or soda, baryta- or lime-water to a silver solution. It is only soluble to a very slight extent in water, the solution possessing an alkaline reaction. It acts as a powerful base, precipitating copper oxide from copper solutions, and partially precipitating the oxides of nickel, lead, cadmium and zinc from solutions of their salts.

Silver suboxide (Ag_4O) is obtained by heating silver salts of organic acids in a current of hydrogen to 100°C; it possesses no metallurgical importance.

Silver peroxide (Ag_2O_2) is produced at the positive electrode when silver solutions are electrolysed, and is also formed by the action of ozone upon silver or its oxide.

Silver Sulphide

Silver sulphide is easily prepared by either dry or wet methods. Prepared in the dry way, by melting together silver and sulphur, it forms a dark grey crystalline mass exactly resembling the native silver sulphide. In the wet way it may be obtained by treating a solution of a silver salt with sulphuretted hydrogen or with sulphides of the alkalies or alkaline earths. Silver sulphide is not fusible alone, but can easily be obtained in the molten state in admixture with the sulphides of other metals (mattes).

Silver sulphide is not decomposed when heated in absence of air, but in presence of air it forms sulphur dioxide and metallic silver. Heated in an atmosphere of steam, metallic silver, sulphuretted hydrogen and sulphur dioxide are produced. Heated in a current of hydrogen, silver sulphide is reduced to metal.

Gaseous sulphur trioxide converts silver sulphide into the sulphate; when in combination with copper sulphide, it can also be converted into sulphate by careful roasting, the copper being left as oxide. In this case the silver sulphate is produced by the action of

[1] *Graham-Otto-Michaelis, Anorg Chemie* 1884, p. 985.

[2] *Trans. A.I.M.E.* xv. p. 423.

sulphur trioxide obtained from copper sulphate, which in its turn is the product of the action of hot air upon the sulphide. Chlorine acts perceptibly on silver sulphide in the cold, and energetically when hot, the silver being completely converted into chloride, and sulphur chloride being produced.

Heated together with sodium chloride in presence of air, silver chloride, metallic silver and sodium sulphate are formed. By roasting with common salt, silver sulphide can be completely converted into chloride even when mixed with other metallic sulphides.

Treated with a solution of cupric chloride, silver sulphide is converted into the chloride, copper sulphide being formed thus :—

$$Ag_2S + CuCl_2 = 2AgCl + CuS.$$

This reaction proceeds most quickly and completely on boiling.

Cupric chloride also reacts in the dry state with silver sulphide, cuprous chloride being produced.

Cuprous chloride solution also reacts with silver sulphide, converting it into chloride according to the equation :—

$$Ag_2S + Cu_2Cl_2 = 2AgCl + CuS + Cu$$

Ferric chloride solution converts silver sulphide only slowly and incompletely into silver chloride. Ferrous chloride and mercuric chloride solutions do not attack it.

Sodium copper thiosulphate ($4Na_2S_2O_3,3Cu_2S_2O_3 + xH_2O$) quickly decomposes silver sulphide, the silver going into solution and copper sulphide being produced (Russell). One part of the solid salt is capable of bringing 0·113 to 0·136 parts of silver into solution. Solutions of the alkalies and alkaline chlorides do not attack silver sulphide, though alkaline cyanides do.

Heated with metallic iron, silver sulphide is completely decomposed with the formation of ferrous sulphide and metallic silver. Iron alone in the cold only acts slowly upon it, but decomposes it more completely in the presence of mercury. It is quickly reduced by iron or zinc in the presence of dilute hydrochloric acid.

Copper, when heated with silver sulphide, partially decomposes it, metallic silver and an argentiferous copper matte being produced. Heated with metallic lead, silver sulphide reacts as follows :—

$$Ag_2S + xPb = Ag_2xPb + PbS$$

but the reduction is not complete, a portion of the silver sulphide uniting with the lead sulphide forming an argentiferous matte. If

lead oxide be present at the same time, then complete decomposition ensues as the latter reacts in this way with the sulphide :—

$$Ag_2S + 2PbO = 2AgPb + SO_2$$

Cupric oxide acts in precisely the same way.

Lead sulphate decomposes silver sulphide according to the equation :—

$$Ag_2S + PbSO_4 = Ag_2Pb + 2SO_2.$$

Silver sulphate decomposes silver sulphide in a similar way. Mercury decomposes the sulphide only slowly, forming silver amalgam, but in presence of metallic iron the decomposition proceeds rapidly, especially on heating.

Silver sulphide is almost entirely decomposed when melted with caustic potash or soda, sulphide and sulphate of the alkali being produced. It is completely reduced by fusion with potassium nitrate.

Molten silver dissolves silver sulphide, according to Percy 100 parts of silver taking up 19·56 parts of the sulphide.

It unites with the sulphides of other metals when melted with them, forming mattes which possess the power of dissolving metallic silver. This fact is made use of in the smelting of argentiferous ores poor in sulphur, where other sulphides, especially iron pyrites, are added to the smelting charge with the object of collecting the silver in the regulus or matte.

By roasting *sweet* the compounds of silver sulphide with the sulphides of iron and copper, a mixture of copper and iron oxides with metallic silver is obtained.

Concentrated nitric acid easily decomposes silver sulphide with the separation of sulphur and the formation of silver nitrate, and strong sulphuric acid acts similarly, forming silver sulphate ; it is not attacked by dilute sulphuric acid.

Dilute hydrochloric acid is without action upon silver sulphide, but it is attacked by the strong acid especially on heating ; silver chloride is produced which partly goes into solution and partly coats the remaining sulphide, interfering with the further action of the acid.

Silver Chloride

This compound may be produced either in the wet or dry way. In the dry way it is formed by the action of chlorine upon either silver or its sulphide, or by the action of hydrochloric acid and certain chlorides upon the same bodies at a red heat. In the wet way it is produced by the addition of chlorine or chlorides to silver

solutions, or by the action of various metallic chlorides upon silver, silver sulphide or compounds of silver with arsenic and antimony.

It is found native as horn silver, crystallising in the regular system. It melts at 260°C. to a reddish yellow liquid, and is slightly volatile at high temperatures. It is soluble to a certain extent in hydrochloric acid and solutions of chlorides, easily soluble in aqueous ammonia and very easily soluble in sodium and calcium thiosulphate solutions and in alkaline cyanides. It is less soluble after fusion than when precipitated from solution and in the latter case the curdy form of precipitate is more easily soluble than the gelatinous, granular or crystalline variety.

According to the investigations of A. Vogel and Bernhart, one litre of a solution of each of the following chlorides at the ordinary temperature dissolves the quantity of silver chloride given in the following table :—

Potassium chloride		0·472	grams of silver chloride.
Sodium	„	0·950	„ „
Ammonium	„	1·575	„ „
Calcium	„	0·930	„ „
Barium	„	0·143	„ „
Strontium	„	0·884	„ „
Magnesium	„	1·710	„ „

In solutions of the chlorides of tin, mercury, copper, zinc, cadmium, nickel and cobalt, it is insoluble.

According to H. C. Hahn and W. M. Curtis the solubility in solutions of various chlorides is as follows :—

Salt.	Strength of Solution. Per cent.	Temperature °C.	Amount of silver chloride dissolved per litre grams.	Silver dissolved per litre grams.
Potassium chloride . .	24·95	19·6	0·914	0·688
Sodium „ . .	25·96	19·6	1·270	0·956
Ammonium „ . .	28·45	30	3·673	2·764
Calcium „ . .	41·26	30	8·350	6·283
Barium „ . .	27·32	30	0·741	0·558
Magnesium „ . .	36·35	30	7·095	5·339
Ferrous „ . .	30·70	20	2·395	1·802
Ferric „ .	37·48	21·4	0·085	0·064
Manganous „ . .	43·85	30	2·958	2·226
Zinc „ . .	53·34	30	0·215	0·162
Copper „ . .	44·48	30	0·833	0·627
Lead	0·99	30	—	—

These experiments, as well as those of Vogel, were performed with amorphous silver chloride, and though the two series do not agree in

all respects, yet they show that silver chloride is more soluble in ammonium, iron and manganese chloride solutions than in solutions of common salt, and more soluble in calcium and magnesium chloride solutions than in any others.

According to Vogel and Bernhart's researches, 11 parts of hydrochloric acid (Sp. Gr. 1·165) dissolve at the ordinary temperature 2·98 parts of silver chloride, the acid diluted with an equal bulk of water dissolves 0·56 parts, diluted with five times its volume of water 0·035 parts, and diluted with an equal bulk of water and at the boiling point 5·6 parts of silver chloride.

Russell has investigated the solubility of silver chloride in sodium thiosulphate solutions; concentrated thiosulphate solutions dissolve more silver chloride than weaker ones, but temperature is without influence upon the solubility, one part of thiosulphate dissolving 0·485 parts of silver chloride containing 0·365 parts of silver. The solubility of the chloride is interfered with by the presence of lead sulphate or sodium sulphate and particularly by caustic alkalies and the alkaline earths.

Silver chloride is reduced to metal by hydrogen as well as by caustic alkalies and alkaline carbonates and the alkali metals. Hydrogen reduces it when it is heated for a long time in a current of this gas. Metals reduce it both in the dry and wet state, and according to Karsten in the following orders, metals with the strongest reducing properties coming first: zinc, iron, arsenic, lead, copper, antimony, mercury, tin and bismuth. Mercury reduces it with the simultaneous formation of mercurous chloride, and in all cases the reduction proceeds more quickly in presence of hydrochloric acid.

Iodide and bromide of silver behave similarly to the chloride.

Compounds of Silver with Arsenic, Antimony and Sulphur.

These are all converted into silver chloride by a chloridising roasting, that is by roasting with common salt. The silver contained in them is also partially converted into chloride by treatment with cupric or cuprous chloride solution.

On fusion with lead and lead oxide, they yield up the whole of their silver, which alloys with the lead.

Of the various oxygen compounds the sulphate, thiosulphate, arseniate and antimoniate of silver are of special metallurgical importance. Silver sulphate is formed when silver is dissolved in boiling concentrated sulphuric acid, and also by roasting such argentiferous metallic sulphides as give rise to the formation of sulphuric anhydride, argentiferous copper matte for example. Silver

sulphate decomposes on heating into silver, oxygen and sulphur dioxide, but the temperature required is higher than that needed for the decomposition of the sulphates of copper, iron and zinc.

Zinc, iron and copper precipitate metallic silver from solutions of the sulphate. Ferrous sulphate also precipitates silver from solutions of the sulphate. Silver sulphate is difficultly soluble in cold water, easily soluble in hot water, and very easily soluble in sulphuric acid. As dilute sulphuric acid is without action on silver it may be separated from its admixture with copper oxide by treatment with this acid, copper sulphate being produced and metallic silver remaining.

Silver nitrate is produced by dissolving the metal in nitric acid; it is decomposed at high temperatures, leaving a residue of metallic silver.

Silver thiosulphate ($Ag_2S_2O_3$) decomposes tolerably quickly in air, forming sulphide and sulphate of the metal, but it forms stable double salts with the thiosulphates of the alkalies and alkaline earths; solutions of sodium and calcium thiosulphates easily dissolve silver chloride forming double salts possessing a sweetish taste.

Sulphuretted hydrogen and sulphides of the alkalies and alkaline earths precipitate silver from its thiosulphate solution in the form of silver sulphide.

Silver arseniate and antimoniate are very stable silver compounds formed in the roasting of arsenical or antimonial silver ores. By melting with lead they are almost entirely reduced, the metallic silver alloying with the excess of lead and by roasting with salt they are almost completely converted into silver chloride.

Sodium thiosulphate or sodium copper thiosulphate dissolves both compounds, one part of the crystallised sodium salt dissolving (best in the hot solution) according to Russell 0·2 parts of silver in the form of arseniate. When present as antimoniate which is also more easily soluble in hot solutions, one part of sodium thiosulphate dissolves 0·05 parts of silver. The solubility of both salts in sodium thiosulphate is considerably increased by the presence of caustic soda.

Mercury does not decompose silver arseniate or antimoniate.

Silver Alloys

The alloys of silver of special metallurgical importance are those with mercury, lead, copper, zinc and gold.

Silver easily alloys with mercury, especially on warming, the alloy being known as silver amalgam. Mercury also possesses the property of reducing metallic silver from its combinations with chlorine, bromine, iodine, sulphur and copper, the reduced metal forming an

amalgam, and it is on this account largely used in the extraction of silver from its ores.

Silver amalgam occurs in nature, crystallised in the regular system.

By squeezing through canvas the fluid amalgam can be separated into two portions, a pasty amalgam which remains behind, and a fluid portion consisting largely of mercury. With amalgams of silver and mercury the upper portions are richer in silver than the lower ones whereas in the case of gold amalgams the lower portions are the richer in gold; this is due to the fact that the specific gravity of mercury is greater than that of silver amalgam but less than that of gold amalgam.

On heating above the boiling point of mercury, silver amalgam parts with its mercury leaving a residue of silver.

Lead alloys very easily with silver when the two metals are simply melted together, and lead possesses the power of withdrawing silver from its compounds with copper, sulphur, arsenic, antimony and from silver salts, forming an alloy with it. This property is made use of extensively for the extraction of silver; from its alloy with copper it is extracted by means of lead, and from its compounds with sulphur, arsenic and antimony by the aid of lead oxide, as these compounds are not completely decomposed by the metal alone. Lead oxide acts as an oxidising agent towards the sulphur, arsenic and antimony, the reduced lead taking up the silver.

From lead-silver alloys the lead can be removed as litharge by oxidation, or it can be separated electrolytically, or the silver can be abstracted from the molten alloy by treatment with zinc which has a greater affinity for silver than is possessed by lead.

Copper alloys easily with silver, and argentiferous copper is produced in the smelting of argentiferous copper ores or when silver and copper ores are smelted together.

Silver can be separated from copper alloys by electrolysis,[1] or if treated with mercury the silver is taken up by the latter metal. If the alloy be melted with lead, a silver-copper-lead alloy is obtained, and if this be heated to a higher temperature than the melting point of lead, a lead-silver alloy flows from it, leaving behind the copper deprived of the greater portion of its silver (liquation).

If the silver-copper alloy be powdered and roasted with common salt, the silver is converted into silver chloride, the copper being then present mainly as oxide. If the alloy be melted with an excess of sulphur, sulphides of both metals are produced (matte), but if an insufficient amount of sulphur is present, it combines with the copper, and silver separates in the metallic state.

[1] See this volume, p. 260.

If the copper-silver alloy be treated with dilute sulphuric acid in presence of air, the copper passes into solution as sulphate, the silver remaining unacted on. With concentrated hot sulphuric acid and with nitric acid both copper and silver go into solution.

Silver readily alloys with zinc, and as zinc possesses a greater affinity for silver than lead, the silver can be extracted from molten silver-lead alloys by its means, A mixture of zinc, silver and lead is produced from which a large proportion of the lead can be separated by liquation. If the lead and zinc are free from copper, a tolerably rich silver-zinc alloy can be obtained, especially by the addition of a small proportion of aluminium. The zinc in the lead-zinc-silver alloy can be got rid of by distillation, or by oxidation or treatment with fluxing materials, or by treatment with sulphuric acid, and from the zinc-silver alloy, the zinc can be eliminated by electrolysis, distillation or treatment with acid.

Gold and silver easily alloy together. If the alloy be boiled with concentrated sulphuric acid, the silver goes into solution as sulphate, the gold remaining behind. Or if an alloy in which the proportion of gold to silver is not greater than 4 : 7 be heated with nitric acid, the silver is dissolved and the gold left; if gold be present in excess of this proportion the residual gold retains some silver. If a gold-silver alloy be treated with aqua regia, the gold dissolves and the silver remains as chloride.

Melted together with antimony sulphide, the silver in a gold-silver alloy combines with the sulphur, and the gold with the antimony. Chlorine gas passed into a molten alloy of silver and gold converts the silver into chloride, the gold being unaffected. By making a gold-silver alloy form the anode and a silver plate the cathode, and using a silver nitrate solution as the electrolyte, silver is deposited on the cathode and gold remains behind at the anode.

The Ores of Silver

Silver occurs in nature both in the free state and in combination with other bodies. In its combinations it occurs either as an essential constituent of the ore or as an accidental ingredient, and both classes of ores are of metallurgical importance. To the first class, the silver ores proper, the following bodies belong:

Native Silver

This often occurs in isomorphous admixture with gold, mercury and copper; it is found at Kongsberg in Norway, in the Erzgebirge

in Saxony (Freiberg, Schneeberg, Johann-Georgenstadt), in the Lake Superior district in Michigan, U.S.A., and in Nevada, in Mexico Batopilas), Peru (Coronel and Loyse mines), Chili, Bolivia, and Australia (Broken Hill, New South Wales).

Amalgam, xAgnHg

The proportions of silver and mercury are variable, the silver content ranging from 26 to 86 per cent. It has been found at Moschellandsberg in the Palatinate, at Rosenau in Hungary, Allemant in France, and in Chili and Bolivia.

Antimonial Silver or Dyscrasite, Ag_2Sb to $Ag_{18}Sb$

This is an isomorphous mixture of silver and antimony with from 64 to 94 per cent. of silver. It has been found chiefly at St. Andreasberg (Upper Harz), Wolfach (Baden), Chanarcillo (Chili), and in Bolivia.

Argentite or Silver Glance, Ag_2S

One of the most important ores of silver, containing 87·1 per cent. of silver and usually small amounts of lead, copper or iron. It occurs, generally in admixture with other sulphides in the Erzgebirge (Freiberg), in Bohemia, Hungary, France (Huelgoët and Chiromagny), Mexico (particularly in the mines at Guanaxuato and Zacatecas), Nevada (formerly in large quantities in the Comstock lode, Virginia City) Peru, Chili, Bolivia (Huanchacas).

Stromeyerite, $(Cu_2S + Ag_2S)$,

with 53·1 per cent. of silver occurs in Chili and in the Altai Mountains, Siberia.

Miargyrite, $Ag_2S + Sb_2S_3$,

with 32·8 to 36·4 per cent. of silver is found in Saxony (Freiberg), in the Harz (Andreasberg), in Bohemia, (Przibram), in Mexico (Potosi, Parenos).

Pyrargyrite (*Dunkles Rothgültigerz*), $3Ag_2S + Sb_2S_3$,

with 59·8 per cent. of silver occurs at Andreasberg in the Harz, in the Erzgebirge, in Norway, Hungary, Spain, Nevada and Idaho and in Mexico and Chili.

PROUSTITE (*Lichtes Rothgültigerz*), $3Ag_2S + As_2S_3$,

with 65·4 per cent. of silver is found at Andreasberg, Freiberg, Spain (Guadalcanal) and Nevada.

FAHL ORE OR TETRAHEDRITE

This is an important silver ore and consists of a mixture of antimony or arsenic sulphide, or both, with sulphides of silver, copper, zinc, iron and mercury. According as to whether antimony or arsenic sulphide is present the ore is distinguished as antimonial fahl ore with the formula $4RS + Sb_2S_3$ or arsenical fahl ore $4RS + As_2S_3$, where R = Cu_2, Ag_2, Zn, Fe, Hg. The silver content varies from a fraction of a per cent. up to 31 per cent., being greatest in the antimonial varieties, the silver in the arsenical varieties being in much smaller amounts or even absent altogether. When the ore contains both arsenic and antimony the silver content seldom amounts to more than 1 per cent. Silver and copper as a rule replace each other, the percentage of copper decreasing with increasing silver content. Fahl ore is found in deposits of silver and copper ores in Germany, the Tyrol, Hungary and Colorado U.S.A.

STEPHANITE (*melanglanz* or *schwarzgültigerz*), $5Ag_2S + Sb_2S_3$,

with 68·4 per cent. of silver occurs in Saxony, Hungary, and Mexico.

POLYBASITE, 9 (Cu_2SAg_2S) $(Sb_2S_3As_2S_3)$

This ore contains 64 to 72·4 per cent. of silver, part of which may be replaced by copper, iron or zinc, whilst the antimony may be partly or wholly replaced by arsenic. It is found at Freiberg, Andreasberg, Schemnitz (Hungary) and in Mexico. Rarer ores are Freieslebenite 5 $(PbAg_2)$ $S + 2Sb_2S_3$ with 22 per cent. of silver, Sternbergite $(AgFe_2S_3)$ with 33 per cent. of silver and silver telluride or Hessite, Ag_2Te, with 61 per cent. of silver.

KERARGYRITE OR HORN SILVER, AgCl,

with 72·5 per cent. of silver frequently occurs in such quantities as to be worth working alone. It is a decomposition product of the sulphide ores, and is found in the upper portions of such deposits in Mexico, Chili, Peru, Bolivia, the Altai Mountains, the state of Colorado (Leadville), U.S.A., Broken Hill, in New South Wales.

BROMITE, AgBr,

with 57·45 per cent. of silver occurs in similar situations to silver chloride in Mexico, Chili, and Broken Hill (Australia).

EMBOLITE, (xAgCl + nAgBr),

with 60 to 70 per cent. of silver is occasionally found under the same conditions as silver chloride, as at Broken Hill.

IODITE, AgI,

with 45·96 per cent. of silver occurs like the chloride in Mexico and Chili and has recently been found at Broken Hill.

The majority of the preceding ores occur together in the several ore deposits, so that the ore delivered to the smelting works is usually a mixture of several of them. The chlorides, iodides and bromides together with native silver, occur in the upper portions of the deposits, whilst the arsenic, antimony and sulphur compounds are found in the lower portions. Fahl ore usually occurs by itself apart from other silver ores.

Minerals which contain silver as an accidental ingredient are galena, zinc blende, copper pyrites, magnetic pyrites, iron pyrites, bournonite, copper glance, bornite, native arsenic, arsenical pyrites and certain nickel, cobalt and bismuth ores.

Galena often contains silver in such considerable amounts (up to 1 per cent.) that the value of the silver in it is greater than that of the lead, and the greater portion of the silver produced in Europe is obtained from galena. Copper ores also often contain a considerable percentage of silver as for instance in the Mansfeld copper schist.

ARGENTIFEROUS PRODUCTS OBTAINED IN SMELTING.

In addition to the ores of silver there are a variety of smelting products which serve as sources of the metal, the chief of these being copper and lead mattes, black copper, argentiferous burnt pyrites and certain drosses and scums.

THE EXTRACTION OF SILVER FROM ITS ORES

It will have been gathered from a perusal of the above list of silver ores, together with the various reactions of silver compounds before described, that there is considerable variety in the processes of silver extraction. In all cases the silver is at last obtained in union with lead, zinc, copper or mercury, or in a solution from which it can be precipitated as metal or as sulphide or chloride, or else it is separated by electrolysis from its combinations. The methods of extraction fall into three main groups:—

1. Dry processes.
2. Wet processes.
3. Electrolytic methods of separation.

To a certain extent the wet and dry methods of extraction are combined, argentiferous products obtained by dry methods being worked up by wet processes or *vice versa*. Electrolytic processes are also usually preceded by a preparation of the ore by dry methods.

The extraction of silver from ores and smelting products in the dry way is based upon the conversion of the silver into a silver-lead alloy, whilst the combined wet and dry methods include:—

I. The conversion of silver into a silver-lead alloy.

II. The production of silver amalgam.

III. The production of a silver compound which is soluble in aqueous solutions.

The electrolytic processes for the separation of silver, require its conversion into a copper-silver, lead-silver, zinc-silver or gold-silver alloy, from which the silver is obtained by making it the anode in an electrolytic cell.

The adoption of any particular method of extraction is determined by the character of the ores or argentiferous smelting products which are to be worked, the various admixtures which they contain and upon local conditions.

Ores very rich in silver are chiefly worked in the dry way. For ores of poor or medium silver content, either wet or dry methods are used, depending on the ingredients associated with the silver compounds, and upon the price of fuel and other local conditions. Ores containing large percentages of lead are mainly worked by dry processes, ores with large amounts of copper being advantageously treated by wet processes or electrolytic methods.

In the case of ores free from copper and lead, or containing only small amounts of these metals, the method of treatment depends upon the price of fuel and motive power, upon the possibility of obtaining lead ores or plumbiferous materials cheaply, upon the possibility of treating the ore directly with mercury without roasting, or of converting the silver in it into chloride, which can then be dissolved by brine or thiosulphate solution. It also depends upon the behaviour of the unroasted ore towards copper chloride solutions, upon the price of the various reagents (salt, copper sulphate, sodium thiosulphate, mercury, sodium sulphide, iron, copper and zinc) as well as upon the arrangements for the transport of the ores, fuel and fluxes to the smelting works.

Argentiferous lead and copper ores are treated by the usual processes for obtaining the respective metals, the silver in lead ores being obtained in the work-lead and in copper ores in the various

intermediate products of copper smelting. It is not possible to give any general description of the methods of working the various metallurgical bye-products for silver, and these processes must be treated individually.

The silver obtained by the above processes is in most cases impure, containing elements (copper, lead, arsenic, antimony, bismuth, selenium) injurious to its use in the arts, and which must therefore be removed by a refining process.

The Extraction of Silver by Dry Methods

The extraction of silver in the dry way is effected by converting the metal into a silver-lead alloy and then submitting this to an oxidising melting in the cupellation furnace. The production of the silver-lead alloy depends upon the power which lead possesses of extracting silver from its ores and from various products containing it, the lead readily alloying with the silver, and the operation is carried out either by a simple melting or by a combination of roasting and melting processes. The process for the combining of the lead and silver is known as the *leading* ("*verbleien*") of the silver, the alloy obtained being called *work-lead*, and the oxidising melting for the separation of the lead is called *cupellation* ("*abtreiben*").

If the amount of silver in the work-lead is not sufficiently great to render direct cupellation profitable, then it is concentrated before being cupelled. This concentration of the silver in the work-lead is effected by two processes, Pattinson's process and the method of desilverising by means of zinc. The various operations involved in obtaining silver in the dry way are then as follows:—

I. The production of work-lead.
II. The concentration of the silver in the work-lead.
III. Obtaining the silver from the enriched work-lead (cupellation).

The process of *leading* is applicable to all varieties of ores and metallurgical products, but it is attended with considerable losses of silver and a large fuel consumption, particularly in the cases of cupriferous ores and of ores and products free from lead and poor in silver. On this account the silver in such bodies is often extracted either by the wet way or by electrolytic treatment.

Leading is used when the ores contain lead, or if free from lead when it is possible to procure cheaply large amounts of lead compounds (litharge, old hearths, &c.), and where fuel is abundant or when the ores are so very rich in silver that they can be put directly into a bath of

molten lead. Its employment in the extraction of silver from argentiferous metallurgical products is limited to those cases where the products are rich in silver or are not suitable for treatment by wet methods; cupriferous products free from lead are in most cases treated most advantageously by means of wet methods or electrolytic processes. Dry methods in all cases demand a fairly cheap fuel.

THE PRODUCTION OF WORK-LEAD

Under this head we have to distinguish:—

1. The production of work-lead from ores.
2. The production of work-lead from metallurgical products, namely, from

a. Matte.
b. Speiss.
c. Alloys.
d. Other metallurgical products.

I. The Production of Work-Lead from Ores.

The leading of the ores is carried out in various ways according to the amount of silver present, and the various admixtures which the ores contain.

Silver ores proper can be divided into those with high, medium, or low silver content.

Ores with a high percentage of silver are thrown into a bath of molten lead, most conveniently in the cupellation hearth or are alloyed with lead by the more costly method of melting them with it in crucibles.

Ores of medium silver content are smelted in blast furnaces with the addition of lead ores or materials rich in lead in order to obtain the silver in the work-lead. If the ores contain sulphur the poorer portions are roasted before smelting, just as lead ores are roasted, whilst richer ores are added directly to the smelting charge. In the case of ores containing sulphur, a matte is always produced which retains some of the silver and which must, therefore, be subsequently worked up for that metal, and as this involves a series of costly operations its formation is to be avoided as far as possible. With cupriferous silver ores like fahl ore the formation of matte cannot be prevented, and in many cases a speiss is produced from which it is even more difficult to obtain the silver than from matte.

Ores poor in silver, if they are free from lead, are not leaded directly, but are converted first into a matte ("*rohstein*"). This is

effected by smelting in blast furnaces with an addition of pyrites if the ores are poor in sulphur, or directly if containing a medium amount, or after previous roasting if rich in sulphur. The matte produced is then leaded. If, however, the ores poor in silver contain some lead, they are smelted direct for work-lead. Argentiferous lead ores are smelted directly for work-lead by the ordinary processes of lead smelting without regard to their content of silver.

Argentiferous copper ores are only leaded when they occur intimately mixed with lead ores or when they are worked in common with cupriferous silver ores like fahl ore. In such cases they are smelted in blast furnaces (after previous roasting if necessary), with roasted lead ores or materials rich in lead such as litharge or cupellation hearths, any silver ores which may be available being added at the same time and the products being work lead and matte. The matte (known as copper matte) contains a considerable amount of silver and is worked up for argentiferous copper matte, from which the silver is extracted by a repetition of the leading process or by wet methods.

This process is only employed in the cases just mentioned, as it is unsatisfactory and costly on account of the imperfect extraction of the silver in the work lead, the considerable loss of metal, and the tedious operations involved in working up the copper matte.

A more satisfactory method and one which is at present generally adopted is to work up the argentiferous copper ores by themselves, collecting the silver in the various intermediate and bye-products of the copper smelting process, and extracting the silver from these by means of wet methods or by electrolytic processes.

Argentiferous zinc ores, when they occur intimately admixed with lead ores as at Freiberg and in the Lower Harz, are either "leaded" direct or after roasting, or they are first distilled to obtain the zinc and the retort residue is then smelted for work-lead, a method which is also in use at Freiberg.

The process of leading was also formerly in use at Joachimsthal in Bohemia[1] for the extraction of silver from nickel and cobalt ores, but on account of the large loss of silver it has given way to wet processes of extraction.

THE PRODUCTION OF WORK-LEAD FROM RICH SILVER ORES

This can be effected either by melting the ores with lead in crucibles or by direct addition of the ore to a red hot bath of the molten metal.

[1] *Berg. u. Hütt. Ztg.*, 1864, p. 104. *Oesterr. Zeitsch.*, 1857, p. 313.

Method of Leading in Crucibles

This method is practically obsolete as it is much more costly than the alternative method. The best plumbago crucibles were used and litharge added as a flux together with some iron if sulphide of silver was present. Potash, glass, borax and soda were also used as fluxes. In this way the conversion of the silver into the silver-lead alloy was fairly complete if there was no production of matte, otherwise the matte retained a considerable amount of silver. If copper were present, a copper matte was produced necessitating a series of costly operations for the extraction of the silver.

This method of leading was formerly in use at Kongsberg in Norway[1] with ores in which 90 per cent. of the silver was in the free state, the ore being melted in charges of about 3 cwt. in plumbago crucibles together with lead, 3 per cent. of iron filings and 1 per cent. of borax, and the silver-lead alloy produced was directly cupelled.

Production of the Silver-Lead Alloy in Lead Baths

The work-lead which has been melted in the cupellation hearths serves as the lead bath and the addition of the silver ores takes place at the commencement of the period of litharge production and after the *abstrich* and first impure litharge have been taken off. The air blast is stopped and the ore is thrown on to the surface of the molten lead in quantities of ½ to 1 cwt., the temperature being raised by increasing the firing. The ore floating on the surface undergoes a partial roasting, and, if arsenic and sulphur are present, these are to a certain extent eliminated, the silver is reduced by the lead and especially by the litharge, and the reduced silver is taken up by the large excess of lead present, any residue remaining on the surface of the bath being fluxed by the litharge. As soon as the slag is fairly fluid it is raked off the surface and the cupellation proceeds until further additions of silver ores are made.

This method is in use at Altenau and Andreasberg in the Upper Harz. At Altenau, ores with more than 2 per cent. of silver are treated in the above way, the ore being added by means of a scoop in quantities of 70 to 90 lbs to a bath of metal weighing about 11 tons, on the hearth of a German cupellation furnace. By quick firing the ore is roasted and then fluxed, and after a short time the residue is raked off, the whole process lasting from ½ to ¾ of an hour, and being again repeated after an interval of from ½ to one hour

[1] *Berg. u. Hütt. Ztg.*, 1855, pp. 49, 99; 1858, p. 101; 1866, pp. 172, 250. *Preuss. Minist. Zeitsch.*, vol. xiv., p. 96.

from the raking off of the residue. Half a ton of ore is added to a lead bath containing 10 tons of lead.

At St. Andreasberg, ores with 10 per cent. and over of silver are treated in the same way, about a cwt. of ore being added each time at intervals of two hours, the lead bath containing at the beginning of the operation 0·4 per cent. of silver. The residue raked off in the process is smelted in blast furnaces with ores containing small or medium percentages of silver.

At Poullaouen in France, ores containing native silver, horn silver and silver sulphide, with 2 per cent. of silver altogether, were also added to the lead bath in the cupellation furnace during the period of litharge formation.[1]

PRODUCTION OF WORK-LEAD ALLOYS FROM ORES OF MEDIUM SILVER PERCENTAGE

Ores with medium percentages of silver and, under favourable circumstances, ores poor in silver, are smelted together with lead ores or with roasted lead mattes, litharge, or other materials rich in lead, as in the ordinary processes of lead smelting. If arsenic, antimony or sulphur are present in the ores, the latter are first roasted unless they contain large percentages of silver. Blast furnaces are generally used for the smelting, reverberatory furnaces being only rarely employed. Generally when the ores contain sulphides, and invariably when they contain both sulphur and copper ores, a matte is obtained in addition to the work-lead ; the matte contains some of the silver and is further worked up to an argentiferous copper matte or to argentiferous raw copper. The production of work-lead in this way in no way differs as regards the plant employed and the methods used, from the ordinary lead-smelting processes previously described.

As most lead ores are argentiferous, an argentiferous work-lead is obtained in the ordinary process of lead smelting, and in many cases silver ores are added to the smelting charge so as to produce a richer work-lead, so that no special description of the leading of such ores can be given, the process being practically the ordinary lead smelting process. The charge is usually made up in such a way that the work-lead produced contains not more than 2 per cent. of silver, otherwise the loss of silver in the slag becomes too great.

The process of leading silver ores is employed at the following places :—At Broken Hill, N.S.W., and Port Pirie, South Australia, where the ores contain chloride and iodide of silver and native silver, at Freiberg in Saxony, St. Andreasberg in the Upper Harz, Schemnitz

[1] *Berg. u. Hütt. Ztg.*, 1859, p. 351.

and Kapnik in Hungary, Colorado, El Paso (Texas) and various Mexican works where sulphur, arsenic and antimony compounds of silver are worked, at Altenau in the Upper Harz, and at the Rothenbacher works near Müsen where cupriferous ores are smelted.

The working of the Broken Hill ore has already been described on page 415. The silver ores proper are chloride, bromide and iodide of silver, embolite and native silver, which occur with kaolin, siliceous gangue and brown haematite, and they are smelted, together with argentiferous lead carbonates in blast furnaces of the American type. In 1891-92 the ores averaged 15 to 18 per cent. of lead and 32 to 39 ounces of silver per ton, and consisted of

51·5 per cent. of Carbonate ores.
47 „ siliceous and clayey argentiferous ores free from iron.
1·5 „ iron ores containing lead and silver.

Limestone and haematite are added to the ore charge to the extent of 32 and 3·1 per cent. respectively, and 50 tons of charge are smelted in 24 hours with a consumption of 18 per cent. of coke, the work-lead produced containing about 300 ounces of silver per ton.

At Freiberg silver and lead ores are smelted together by the roasting and reduction process, the methods being described more in detail on page 386. The lead ores are galenas containing on an average 40 per cent. of lead and 0·15 per cent. of silver, the amount of silver in the ores to be leaded ranging from 0·005 up to several per cent. These ores consist of silver ores proper (*"dürrerzen"*), argentiferous copper ores with from 1 to 10 per cent. of copper, argentiferous zinc blendes with less than 25 per cent. of zinc and argentiferous mispickel and pyrites. Argentiferous zinc blendes with more than 25 per cent. of zinc are first distilled to obtain the zinc and the residue is added to the smelting operation. A portion of these ores is either distilled in order to obtain arsenic and arsenical compounds, or roasted for the manufacture of sulphuric acid. The residue from this together with the other raw ores and galena is then roasted in a long-bedded calciner (*fortschaufelungsofen*), certain residues containing lead and silver, and flue-dust with less than 25 per cent. of arsenic being added at the same time. The charge for roasting is so constituted as to contain 20 to 30 per cent. of lead, 20 per cent. of sulphur, 20 to 25 per cent. of silica and not more than 10 per cent. of zinc, the silver content varying from 0·01 to 0·015 per cent. This roasting, the material being finally melted, brings the sulphur content down to 3 to 5 per cent., this amount of sulphur serving to convert the copper present into matte in the subsequent smelting. Some

twelve tons of ore are roasted in 24 hours with a consumption of 35 per cent. of coal.

The roasted mass is then smelted in Pilz furnaces together with an equal weight of slag from a previous operation, and in this way a work-lead with 0·5 to 1 per cent. of silver is produced together with lead matte with 15 to 20 per cent. of lead, 8 to 14 per cent. of copper and 0·14 to 0·2 per cent. of silver, which matte is subsequently smelted for copper matte and work-lead.

At the works at St. Andreasberg in the Upper Harz foreign silver ores with 10 per cent. of silver are smelted together with argentiferous lead ores which have been roasted in a reverberatory furnace, litharge and old hearths, the combined roasting and reduction and iron-reduction processes being employed. Formerly ores with less than 1 per cent. of silver were roasted together with the galena, whilst ores with more than 1 per cent. were added to the charge in the raw state. At present richer silver ores, up to 4 per cent. are roasted. The smelting operation is carried on in Raschette furnaces such as those described under lead smelting, in old furnaces of trapezoidal section and in circular furnaces with boshes, basic fluxes (roasted matte, slag from matte smelting, burnt pyrites, basic iron slags, limestone) and slags from a previous operation being used.

The ore charge is so constituted that the work-lead produced contains about 2 per cent. of silver, the matte containing 0·5 to 0·8 per cent. of silver, 10 to 15 per cent. of lead and 7 to 15 per cent. of copper, whilst the slag produced lies between a mono- and bisilicate and contains 2 to 5 per cent. of lead and 0·008 to 0·02 per cent. of silver.

The matte is roasted in kilns (9 feet high, 4 feet 6 inches long and 4 feet deep) and is put back into the lead smelting operation until the amount of copper in it reaches 15 per cent., when it is worked up by itself for this metal. It is first roasted in kilns and then smelted with litharge and slag from the ore smelting, producing a work-lead with 0·3 per cent. of silver and a matte with 0·1 per cent. of silver, 10 per cent. of lead and 25 per cent. of copper. The matte is then roasted in kilns and re-smelted without any addition of litharge, the matte obtained in this way containing 35 per cent. of copper. This is treated at the copper works where it yields a raw copper with 0·2 per cent. of silver.

The slags are smelted with a certain amount of matte yielding work-lead with 0·4 to 0·5 per cent of silver, matte with 0·1 per cent. of silver, 9 per cent. of lead, 10 to 20 per cent. of copper and a clean slag containing 0·5 per cent. of lead and 0·001 to 0·002 per cent. of silver. This work-lead serves as the bath into which the rich silver ores

are put. The matte is roasted and added again to the slag smelting, until it is comparatively poor in lead and rich in copper when it is worked up for the latter metal.

At Schemnitz in Hungary auriferous silver ores are worked up together with lead ores. The lump silver ores contain the silver chiefly as sulphide (silver glance Ag_2S), and they contain 30 to 97 per cent. of silica, up to 20 per cent. of alumina, and up to 30 per cent. of calcium carbonate together with from 0·05 to 2 per cent. of manganese oxide and carbonate. The average amount of auriferous silver is 0·15 per cent., and the amount of gold in the silver varies from 0·03 to 12 per cent. The silver ores in the state of slimes contain 0·06 to 1 per cent. of silver and 0·01 to 0·4 per cent. of gold.

The lead ores used for leading are quartzose cupriferous pyrites and pyrites containing galena with an average lead content of 45 per cent. and 0·5 to 10 per cent. of copper, the copper content being the greater, the poorer the ores are in lead. The lead ore slimes contain 0.02 to 0·08 per cent. of silver and in this silver there is 0·014 to 0·28 per cent. of gold. The ores are first roasted in a long-bedded calciner (*fortschaufelungsofen*), 66 feet long and 16 feet wide, the roasted ore being fused at the end of the operation. The charge is adjusted so as to contain 10 per cent. of lead, 20 per cent. of sulphur and 200 parts of lead for every one part of silver. So much iron is added in the shape of pyritic gold and silver ores, burnt pyrites and brown haematite that the fused mass shall be practically a monosilicate. Every 24 hours, 12 to 13 tons of charge are roasted, with a consumption of 353 cubic feet of wood for 10 tons of roasted ore. Four workmen are required in each shift, and the product is an iron-lead monosilicate with 2·5 per cent. of sulphur and at least 10 per cent. of lead containing more than 5 per cent. of auriferous silver.

The roasted ores are smelted in Pilz furnaces with Arents's automatic taps and eight tuyeres, each 1·2 inches in diameter, worked with a blast pressure of half an inch of mercury. The modern furnaces are 4 feet in diameter at the tuyere level and 5 feet at the throat, the distance between tuyere level and throat being 11 feet 6 inches. In the year 1886 the charge consisted of 9 cwt. of roasted ore, 66 lbs. of furnace products containing lead and 2 to 4 cwt. of slag from a previous operation; and in 1893 it was composed of 8¼ cwt. of roasted material, 22 lbs. of rich ores, 44 lbs. of roasted matte, 44 lbs. of raw matte, 22 lbs. litharge, 22 lbs. scums, 44 lbs. ironstone, 22 lbs. scrap iron, 3½ cwt. slag, and 22 lbs. of old hearths. The average weight of the charge was 14 cwt. and 1 cwt. of coke was used for smelting this amount, 65 to 70 charges (45·5 to 49 tons) being

smelted in 24 hours. The furnace is worked in 12-hour shifts with two charges and four smelters. The products of the smelting operation are work-lead with 0·5 to 1 per cent. of silver, matte with 12 to 15 per cent. of lead, 8 to 10 per cent. of copper, and 0·1 to 0·3 per cent. of silver (with 0·001 to 0·002 per cent. of gold) and slag with 3 to 4 per cent. of lead and 0·0035 to 0·015 per cent. of silver.

The slags are smelted together with matte in Pilz furnaces yielding a second matte, the charge in 1893 consisting of 9½ cwt. of slag, 22 lbs. of poor ore, 1 cwt. of raw matte, 88 lbs. of roasted matte, 22 lbs. of litharge, 22 lbs. of slag from reduction of litharge, 22 lbs. of old hearths, and 22 lbs. of liquation residues. Every 24 hours 50 to 55 charges were worked with a blast pressure of $\frac{5}{16}$ to $\frac{7}{16}$ of an inch of mercury, and a consumption of 1 cwt. of coke to every 12½ cwt. of charge. The products were work-lead with 0·3 per cent. of silver, matte with 1 per cent. of lead, 25 per cent. of copper, and 0·07 to 0·08 per cent. of silver, together with a waste slag containing 1·5 per cent. of lead and 0·002 per cent. of silver.

The matte is then smelted and produces work-lead with 0·5 per cent. of silver and argentiferous copper matte.

At Kapnik, in Hungary, argentiferous and auriferous pyritic slimes are leaded with argentiferous galena. The slimes are separated into rich gold slimes with 0·015 per cent. of auriferous silver (33 per cent. of gold), and into so-called "*ärarische*" pyritic slimes with 0·09 to 0·1 per cent. of auriferous silver containing, however, only 1·2 per cent. of gold.

The lead ores contain 45 to 60 per cent. of lead and 0·9 to 1 per cent. of auriferous silver (1 to 3·2 per cent. of gold). The pyritic slimes at the time of the author's visit in 1887 were still being roasted in heaps, whilst the lead ores were roasted in long-bedded reverberatory furnaces, the roasted ore in each case being smelted in blast furnaces with roasted matte, the charge consisting of

73	parts by weight	of	roasted pyritic slimes
16	„	„	„ lead ores
11	„	„	quartzose flux
26	„	„	roasted matte from a previous operation.

The products were work-lead with 0·25 per cent. of auriferous silver (10 per cent. of gold in the silver), and matte with 0·04 to 0·05 per cent. of auriferous silver, 12 per cent. of lead, and the whole of the copper in the charge.

The matte is roasted in three separate firings, and part of it is added to the ore charge, part of it being smelted with additions of

quartzose silver ores and plumbiferous materials in blast furnaces. In this latter operation work-lead and a plumbiferous copper matte are obtained, the latter being deprived of its silver by being leaded, after which it is worked up for copper. The work-lead obtained in the leading of the matte has less than 0·15 per cent. of auriferous silver and consequently is submitted to the zinc desilverising process.

At the smelting works at Colorado, which have already been described under the heading of Lead, silver ores proper are smelted together with lead ores, partly by the roasting and reduction process and partly without any previous roasting.

At the works of the Consolidated Kansas City Smelting and Refining Company at El Paso in the State of Texas, silver ores from Tombstone, Arizona, are smelted together with carbonates from Sierra Mojada in Mexico (see page 414).

At Altenau in the Upper Harz, cupriferous silver ores with less than 2 per cent. of silver are smelted in a Raschette furnace together with roasted lead ores producing work-lead and matte.

Silver ores with more than 1 per cent. of silver are smelted direct, whilst ores with less than 1 per cent. of silver are first roasted in long-bedded reverberatory furnaces. The silver ores are smelted together with roasted and raw matte from a previous operation, burnt pyrites, roll scale, or similar ferruginous material, small amounts of limestone, plumbiferous materials, and slags from a previous operation. The furnaces are worked with a blast pressure of 1 to 1½ inches of mercury, and a Raschette furnace produces 2 to 3 tons of work-lead in 24 hours and a similar amount of matte, the consumption of coke being 30 to 40 per cent. of the weight of the charge. The composition of the charge is so regulated that the work-lead obtained does not contain more than 2 per cent. of silver. The matte contains 0·15 to 0·4 per cent. of silver as well as the whole of the copper contents of the charge and it is added, partly raw, partly after roasting, to the ore smelting charge until its copper content is raised to 10 per cent.

The roasting of the matte is effected in kilns, and in 24 hours 1·25 tons are roasted down to 7 per cent. of sulphur, two men attending to a group of four kilns in the 12 hours shift.

The roasted matte with more than 10 per cent. of copper is smelted in blast furnaces with the addition of various lead-containing materials and slags, the products being work-lead and copper matte. The copper matte contains 0·05 to 0·2 per cent. of silver, 9 to 14 per cent. of lead, and 25 to 40 per cent. of copper. It is roasted in kilns and then concentrated in blast furnaces ("*brillenöfen*," see page 94), whereby black copper (with 10 per cent. of lead and 60 to 70 per cent. of

copper) and a concentrated copper matte with 0·1 to 0·3 per cent. of silver, 1 to 3 per cent. of lead and 70 per cent. of copper are obtained. This concentrated matte is roasted sweet in a long-bedded calciner (treating 3·75 tons in 24 hours, and using 0·75 tons of coal) and then smelted in blast furnaces for black copper containing 85 to 94 per cent. of copper and 0·2 to 0·3 per cent. of silver. The black copper is desilverised by wet methods. The slags from the matte smelting are added to the ore smelting on account of their basic properties, whilst slags from ore smelting are added to the matte smelting charge.

When large quantities of ore slags have accumulated they are worked up for the lead and silver they contain (2 to 3·5 per cent. of lead and 0·015 to 0·03 per cent. of silver), undergoing a special slag smelting together with matte, basic slags, and plumbiferous materials, the products being a waste slag with 0·001 per cent. of silver, 1 to 1·5 per cent. of lead and 12 to 15 per cent. of zinc, together with a matte and work-lead.

At the Rothenbach works near Müsen, in the district of Siegen, roasted argentiferous copper pyrites, fahl ores, and roasted galena were smelted in blast furnaces for work-lead and argentiferous and cupriferous lead matte. Formerly 6 parts of fahl ore, 10 of lead ore, 10 of ore slag, and a little iron finery slag (or in default of lead ores 3 parts of litharge were used to every 10 of fahl ore) were smelted together and the cupriferous lead matte obtained was leaded in order to desilverise it, and lastly it was worked up for raw copper.

THE PRODUCTION OF WORK-LEAD FROM POOR SILVER ORES

If the poor ores contain lead they are treated similarly to the ores with moderate percentages of silver. If, however, they are free from lead and very poor in silver, they are not leaded direct, but, with the object of enriching them, they are smelted with materials containing sulphur so as to yield a raw matte. This, consisting chiefly of sulphide of iron, is capable of dissolving silver. In very rare cases the raw matte before being leaded undergoes a roasting and second smelting with the object of increasing its silver content (Kongsberg in Norway).

If the silver ores contain pyrites, they are either smelted direct or after roasting if the pyrites is present in excess, pyrites being added if the ores are deficient in sulphur.

The smelting for raw matte is mainly conducted in blast furnaces and only rarely in reverberatory furnaces, and in the smelting operation the foreign metallic oxides and earthy matters are fluxed and

the silver is collected together into the matte. The materials in the charge are so proportioned that the matte shall not contain more than 2 per cent. of silver, otherwise too much silver finds its way into the slag, which in any case contains some mechanically entangled matte. The leading of the matte is then proceeded with in the ordinary way and will be further described when treating of the leading of argentiferous mattes.

The working up of argentiferous ores for raw matte in this way is carried on at Kongsberg in Norway, at Fernezely near Nagybanya in Hungary, at Zalathna in Transylvania, and at the Gavrilov smelting works in the Altai.

At Kongsberg,[1] silver ores with 0·03 per cent. of native silver with a gangue of quartz and calcium carbonate are smelted in blast furnaces 15 feet high. Pyrites and magnetic pyrites containing some copper are added to the charge, iron finery slag is used as a flux, and coke and charcoal as fuel, the product being a raw matte with an average silver content of 0·18 to 0·3 per cent. and a clean slag containing 0·002 to 0·006 per cent. of silver. The raw matte which is run off into a tapping pot, where it solidifies and is taken out as a cake, is not at once leaded but first undergoes a process of concentration. For this purpose it is broken into pieces the size of nuts and then roasted four times in stalls, after which it is smelted for matte with rich ores containing 1 per cent. of silver and argentiferous flue dust, the enriched matte being then leaded as subsequently described.

At Fernezely and Strimbul in Hungary gold and silver ores are smelted in blast furnaces for raw matte which is afterwards leaded. At the Fernezely works the ores are "*dry ores*" (*durrerze*), lump pyrites and pyritic slimes. The *dry* ores are free from lead and pyrites, and contain their silver in the form of pyrargyrite, and the gold either free or as a gold-silver alloy. The percentage of silver is about 0·125 and the silver produced contains 4 to 8 per cent. of gold. The lump pyrites contains the silver as proustite and the gold in the free state, the silver percentage varying from 0·03 to 0·12 and the silver carries 10 per cent. of gold. The pyritic slimes are richest in gold; they contain 0·2 to 0·14 per cent. of auriferous silver containing 20 per cent. of gold. The pyrites is roasted before smelting, and at the time of the author's visit the richest slimes were roasted in Bode's shelf furnaces, the bulk of the slimes as well as the lump pyrites being still roasted in heaps, though it was intended to use the shelf furnaces for the whole of the ores.

The ores undergo only one roasting in heaps, the heaps consisting

[1] Percy, *Silver and Gold*, I. 1880, p. 507; Kerl's *Metallhüttenkunde*, p. 259.

of three layers of a mixture of lump ore and slimes, which are arranged alternately with layers of wood and charcoal, the heaps containing from 120 to 240 tons of ore. For every 10 tons of ore 405 cubic feet of wood and 175 cubic feet of charcoal are used.

The roasted ores are smelted for raw matte in blast furnaces of circular section 26 feet high, having a diameter of 5 feet 8 inches at the throat and 5 feet 2 inches at the tuyeres. The charge consists of 90 parts of roasted pyrites, 5 parts of *dry* ores, and 12 to 13 parts of limestone, charcoal being used for fuel. The blast is supplied under a pressure of 1 inch of mercury and 3 tons of charge are worked in 24 hours, 840 cubic feet of charcoal being used for every 10 tons of charge.

The yield of matte is 33 per cent. of the weight of the ores and this contains 90 per cent. of the auriferous silver originally present in the ore, the remaining 10 per cent. being found in the slag, which is a monosilicate and is chiefly used up in the smelting for the leading of the matte.

At the Zalathna works in Transylvania at the time of the author's visit in 1887, auriferous and argentiferous pyrites with a highly siliceous gangue were being worked. The gold was almost all present in the free state and only a small portion was combined with tellurium, and the silver was partly present as sulphide and partly alloyed with the gold.

The pyritic slimes which formed 92 per cent. of the ores delivered at the works were classed as poor, medium, and rich slimes, the poor varieties containing 0·01 to 0·029 per cent. of auriferous silver, the medium 0·03 to 0·05 per cent., and the rich over 0·05 per cent.

The richest ores, which were, however, only procurable in small quantities, were the tellurium ores, of which there were two varieties, one with 1·5 to 5 per cent. of auriferous silver, and ores of the second class with 0·2 to 1 per cent.

The slimes were still submitted in part to an imperfect single roasting in heaps, and in part were roasted in Bode's shelf furnaces. The heaps were made up of 200 to 250 tons of ore and burnt for 4 or 5 months, 10 tons of ore requiring 166·5 cubic feet of wood.

The shelf furnaces (Malétra furnace) possessed 5 or 7 shelves, and 1 cwt. of slimes was placed on each shelf, 16 cwt. of slimes with 36 per cent. of sulphur being roasted in 24 hours down to 6 per cent. of sulphur. The gases from the roasters were partly utilised for sulphuric acid making, and partly for conversion into sulphur with the aid of sulphuretted hydrogen.

The average composition of the roasted slimes was as follows:—

Sulphur . .	6·28 per cent.	Silver . .	0·012 per cent.
Iron . . .	56·45 „	Gold . .	0·0044 „
Manganese .	1·73 „	Calcium .	0·024 „
Copper, Zinc	traces	Aluminium	2·25 „
		Silicon . .	19·90 „
		Oxygen .	18·15 „

The ore was then smelted in circular blast furnaces 23 feet high, provided with wells or sumps and having a diameter of 39 inches at the throat and of 35½ inches at the tuyere level.

The slimes which have undergone heap roasting are sintered together in the process, and do not require any binding material, but the slimes roasted in the shelf furnace must be agglomerated by means of milk of lime before smelting.

For fluxing the iron, acid slags were added and quartzose ores if available. The richest gold ores were added to the smelting process without previous roasting, and the average composition of the charge to be smelted was as follows in 1886:—

30 to 33 per cent.	roasted slimes from the shelf furnace
11 „	„ „ heap roasting
8 „	unroasted rich slimes
14 „	poor ores and roasted matte
30 to 33 „	slags from a previous operation or from the leading process.

Charcoal was used as the fuel with blast at a pressure of $\frac{6}{16}$ to $\frac{7}{16}$ of an inch of mercury, 7 tons of charge, equivalent to 4·54 tons of ore, being worked in 24 hours with a consumption of 7·3 cubic feet of charcoal for every 2 cwt. of ore.

From 100 parts of roasted ore, 48 parts of raw matte of the following average composition were obtained:—

Iron	65·86	Silver	0·028
Calcium . . .	0·04	Gold	0·011
Zinc	traces	Sulphur . . .	28·54
Lead	4·23	Slag	1·29

The slags lay between mono- and bi-silicates and were composed as follows:—

Silica	41·6	Magnesia	0·24
Ferrous oxide . .	49·95	Alumina	3·42
Manganous oxide .	0·82	Sulphur	1·02
Lime	2·66	Silver	0·0007
		Gold	0·0001

The process for the leading of the matte will be subsequently considered (see page 491).

At the Gavrilov works in the Altai, Tomsk,[1] situated 200 verst north-east of Barnaul, ores are worked containing 0·027 to 0·03 per cent. of silver and 0·5 per cent. of lead. The ores are smelted in blast furnaces to a raw matte which is desilverised by treatment with molten lead in hearths. The ores have a gangue of quartz, heavy spar, oxide of iron, and a little lime and magnesia, and contain some iron pyrites. They are divided into ochreous quartzose ores with from 42 to 75 per cent. of silica, 22 to 40 per cent. of heavy spar, 5 to 15 per cent. of ferric oxide and alumina, and 3 to 5 per cent. of lime and magnesia, into ochreous sparry ores with 10 to 29 per cent. of silica, 5 to 7 per cent. of lime and magnesia, 52 to 85 per cent. of heavy spar, 3 to 17 per cent. of oxide of iron and alumina, and into sparry pyritic ores with 6 to 35 per cent. of silica, 47 to 84 per cent. of heavy spar, and 4 to 17 per cent. of metallic sulphides (pyrites).

The ores are smelted with coke in two- and three-tuyered blast furnaces, yielding a raw matte which is remarkable for its high percentage of barium sulphide (up to 40 per cent.). The heavy spar in the ore partly reacts with the silica forming sulphur tri-oxide and barium silicate, and it is partly reduced to sulphide and passes into the matte. In consequence of their high specific gravity, owing to the barium they contain, the slags will not easily separate from the matte, so that if the charge be at all wrongly composed, mixtures of matte and slag are obtained which must be again added to the ore smelting process. The best composition for the charge is as follows:—

Quartzose ochreous ores	25 to 30 per cent.
Sparry pyritic ores / Sparry ochreous ores	75 to 80 „
	100 parts
Desilverised raw matte	10 to 12 per cent.
Iron ores	3 „
Lime	5 „
Slag from matte desilverising	5 „
Impure slag from ore smelting (mixtures of matte and slag)	25 „

In normal working, raw matte is obtained with 0·14 to 0·17 per

[1] Jossa and Kurnakoff, *Die Blei- Silber und Kupferhüttenprozesse im Altai. Berg. und Hüttenm.-Ztg.*, 1886, Nos. 16, 17, 18, 19.

cent. of silver, and the composition of the matte which, owing to its barium content is unique, is as follows :—

	I.	II.	III.
Sulphur	24·29	27·74	25·70
Barium	35·33	35·62	39·66
Iron	20·38	24·97	20·42
Copper	6·66	5·10	6·25
Zinc	2·73	1·66	2·54
Lead	0·21	0·51	traces
Aluminium	0·47	0·62	traces
Calcium	0·89	0·44	1·51
Magnesium	1·43	0·41	1·52

The slag is very acid and approximates closely to a trisilicate, having the following composition :—

	I.	II.	III.
Silica	45·502	44·978	44·30
Barium oxide	41·856	40·868	44·42
Sulphur	1·773	2·035	1·37
Ferrous oxide	7·394	6·180	3·38
Alumina	3·650	3·382	3·42
Lime	2·02	2·742	3·21
Magnesia	0·623	0·722	1·98

The entire process is imperfect; the working of the matte is described further on.

A similar method of working siliceous ores is in use at Pavlov's works 50 versts west of Barnaul, with this difference that the ores are roasted in heaps before smelting, and the matte produced is desilverised by means of a bath of molten lead.

II. THE PRODUCTION OF WORK-LEAD FROM METALLURGICAL BYE-PRODUCTS

Matte, speiss, alloys, and similar metallurgical products are leaded for the purpose of extracting the silver they contain.

The Leading of Mattes.

Argentiferous mattes are produced during the leading of silver ores, in the smelting of argentiferous lead and copper ores, and as shown above they are produced during the smelting of poor silver ores for the purpose of enriching them in silver before they are leaded.

The leading of argentiferous mattes is effected either by (1) introducing the matte into a bath of molten lead or (2) by smelting the matte in blast furnaces with materials rich in lead, such as litharge, old hearths, lead carbonate, or roasted galena.

(1) *Leading in a bath of molten lead.* (*Eintränken* or "lead soaking" process.) This process has for its object the decomposition of the silver sulphide in the matte by means of metallic lead, the separated silver alloying with the excess of lead. As, however, silver sulphide is not completely decomposed by lead, the matte cannot be completely desilverised by a single operation. By bringing the matte and lead into as intimate contact as possible, and by repeating the process several times, the greater part of the silver can, however, be extracted from the matte. In the United States (Pueblo in Colorado) where this process is carried out, the limit of extraction has almost been reached. This process yields as a rule a less complete extraction of the silver than the method of smelting the matte with plumbiferous materials, and it is therefore only occasionally employed and only in conjunction with the process of leading the matte in blast furnaces.

The matte is either run directly from the blast furnace in its molten condition into a lead bath, or else the matte is melted in a hearth, and lead is added to it, when it melts and sinks through it, or the molten matte is allowed to rise through a column of molten lead, or lastly, the lead is melted in a reverberatory furnace, and the matte to be desilverised is added to the metallic bath in a powdered condition, and does not reach the fusing point.

The first method is in use at Kongsberg in Norway, the second at the Gavrilov and Pavlov works in the Altai. The third method has been tried experimentally at Lohe near Siegen, and the last method, the so-called Crooke process, is in use at Pueblo, Colorado.

At Kongsberg in Norway, the concentrated matte, the composition of which has already been given, is allowed to flow from the blast furnace into a tapping hearth, where lead is added to it in the proportion of 3 parts of lead to every 10 parts of matte.

As soon as the lead is melted, the fluid mass is intimately mixed by stirring with an iron rod. The matte and lead are then allowed to separate, which they do by reason of their different specific gravities, and the matte is lifted off after cooling. The matte now contains 0·75 to 1 per cent. of silver and the lead 5 per cent., and the desilverising is the more perfect the higher the temperature of the matte when the lead is introduced. The partially desilverised matte is smelted with additions of plumbiferous material in blast furnaces in order to further desilverise it.

The second method is employed at the Gavrilov and Pavlov works in the Altai Mountains. The raw matte, the composition of which has already been given, is melted in a hearth heated by coal and worked with a blast of air, the hearth bed consisting of a mixture of clay and charcoal dust. When melted, the slag is raked off the surface of the bath, which is then covered with charcoal, and upon this the lead for desilverising is put in the form of small bars. These bars melt and the molten lead falls through the molten matte to the bottom of the hearth, carrying with it the greater part of the silver contents of the matte. In order to ensure a thorough mixture of the lead and matte, a pole of green wood is thrust to the bottom of the hearth and allowed to remain there for about three minutes, the commotion caused by the evolved gases ensuring intimate admixture of the lead and matte. After the wood is withdrawn the lead settles down to the bottom of the hearth and is run out through a tap hole which is closed as soon as matte begins to issue from it.

The matte is treated four times in this way with lead. The lead from the first operation is cupelled, whilst the lead from the succeeding three operations is used over again for desilverising. By these operations the silver content of the matte is reduced from 6 solotnik per pud to 1 to 1·5 solotnik (1 pud = 36 lbs. avdps. = 3,840 solotnik). The desilverised matte and the slags are added to the ore smelting charge. The lead loss is returned as 16 parts of lead for every unit of silver obtained, and the loss of silver amounts to 6 per cent. of the silver content of the matte. A hearth yields 150 to 160 pud of work-lead in 24 hours, and the concentrated work-lead contains 0·32 per cent. of silver.

The third method, or the hydrostatic process, which consists in allowing the molten matte to pass up through a column of molten lead has not proved a success, as the matte is not completely desilverised, and it is moreover costly, as it necessitates the use of a special furnace for melting the matte. Menzler, in his trial of this method at the Lohe works in Siegen, used a low blast furnace (*krummofen*) with a deep well in the forehearth, the forehearth being divided into two portions by a partition wall of firebrick reaching nearly to the bottom. Molten lead was run into the well, and the molten matte flowing out of the furnace forced the lead into one of the divisions of the well, and then the matte forced its way up through the column of molten lead and formed a layer on its surface. According to Karsten,[1] not more than five-sevenths of the silver content of the matte can be obtained in this manner.

[1] *System der Metallurgie*, part 5. p. 521.

The method of desilverising matte by throwing it in a powdered condition into a lead bath was in use at the time of the author's visit (1892) at the Pueblo Smelting and Refining Company in Colorado.

The lead, in quantities of twenty-five tons, was melted in a reverberatory furnace similar to that used in refining. Crushed copper matte was then strewn on the surface of the molten metal and allowed to remain for an hour. It is essential to success that the metal bath be fairly cool, so that the matte shall not fuse, otherwise the lead abstracts copper from the matte, and a part of the silver passes back into the fluid matte. The bath is kept cool by iron bars, fastened to the bottom of the bath, so that the matte does not melt but at the most reaches the softening point.

In the first treatment of the matte, 75 to 80 per cent. of its silver content is obtained in the lead, and a further treatment is necessary to obtain the rest of the silver. Formerly the matte underwent four successive operations, but in 1892 a second operation was found to be sufficient. The plant consists of four terraced reverberatory furnaces lying at different levels, and each holding 25 tons of lead, the lead flowing from the upper to the lower one, and the matte, in charges of 1½ tons, travelling in the opposite direction.

Into the top reverberatory furnace, poor lead or lead free from silver is put, whilst the enriched lead containing also 2 to 3 per cent. of copper is tapped out of the lowest furnace. The fresh copper matte is brought into the lead in the lowest furnace, whilst the partially desilverised matte is put on to the fresh lead in the top furnace, and leaves it almost free from silver but containing some lead. The process lasts 1½ hours in each furnace, and according to the manager's statement the desilverised matte contains less than one ounce of silver per ton. The desilverised matte is then worked up for refined copper. It is first smelted in blast furnaces to free it from mechanically-entangled lead which solidifies below the matte, the lead content of which is thus reduced to 15 per cent. The matte is then roasted, first in a long-bedded calciner and then at a higher temperature in a reverberatory furnace worked with an air blast (O'Harra-Brown furnace, see copper, p. 72), the lead contents being converted in this way into oxide and sulphate, the matte not being melted in the process. The roasted matte is then smelted in an English reverberatory furnace, together with quartz, for black copper, the lead oxide and sulphate being converted into a silicate slag by the quartz, this slag being added to the lead ore smelting charge, and the black or blister copper, containing about 99 per cent. of the metal, being lastly refined in an English reverberatory furnace. . .

This process is fairly complicated, so that its economic success seems doubtful, and the author was not made acquainted with the results obtained.

Smelting of Matte with Materials containing Lead.—By smelting matte with materials containing lead, such as lead ores or plumbiferous metallurgical products, the lead is reduced and alloys with the silver of the matte. The matte cannot however be completely desilverised by a single operation. In addition to work-lead a matte poor in silver is produced, which is, as a rule, roasted and then smelted again with plumbiferous material, and by a repetition of this process the matte can be deprived of most of its silver, provided it be not too rich in copper. Smelting with lead products from the cupellation process, such as litharge and old hearths, is particularly favourable to a good extraction of the silver. Cupriferous mattes must be repeatedly treated in the above way in order to extract their silver, and it is consequently better, as a rule, to work such mattes by a wet process or electrolytically. Mattes containing both copper and lead are treated as in the leading of cupriferous silver ores and in the smelting of argentiferous copper ores containing lead, the object being to separate the lead they contain by one or several roastings and smeltings, the copper matte which is obtained being then either worked up by wet processes, as at Freiberg, or else smelted in the dry way for blister copper, the silver contents of this being subsequently extracted either in the wet way or by electrolytic processes.

The leading of mattes in this way is performed at Fernezely Kapnik and Strimbul, in Hungary; at Zalathna, in Transylvania; at the Rothenbacher works, near Müsen; and at the works in the Upper Harz, and at Freiberg.

At the Fernezely works, in the mountain district of Nagy Banya, in Hungary, the following method was adopted at the time of the author's visit.

The raw matte was twice roasted in heaps and then smelted, together with roasted lead ores and rich quartzose roasted ores. The roasting of the lead ores was conducted in a long-bedded calciner with a single hearth 62 feet long and 8 feet 3 inches broad. The smelting was conducted in a furnace exactly similar to those in use for ore smelting, the charge being composed as follows:

62 parts of roasted lead ores
30 „ „ matte
8 „ rich quartzose ores.

The additions of the materials containing lead were so arranged

that for every part of auriferous silver in the charge 200 to 250 parts of lead in the form of litharge or old cupellation hearths were added. Charcoal served as fuel and reducing agent, the blast pressure was $\frac{1}{2}$ to $\frac{11}{16}$ of an inch of mercury, and every 12 hours two tons of charge were worked off, 735 cubic feet of charcoal being used for every ten tons worked. The products were work-lead with 0·3 to 0·7 per cent. of silver, and a matte with 0·08 per cent. of silver, 10 to 12 per cent. of lead, and 1 per cent. of copper, 80 per cent. of the lead in the charge being obtained in the form of work-lead, the rest being in the matte and the slag. The matte produced amounted from 15 to 16 per cent. of the charge. The matte was then twice roasted and smelted with plumbiferous materials in order to extract what silver it contained, and to enrich it in copper. The smelting was conducted in a blast furnace with sump 19 feet 6 inches high, 3 ft. 10 in. diameter at the throat, and 3 ft. 3 in. at the tuyere level, air at a pressure of $\frac{9}{16}$ to $\frac{11}{16}$ of an inch of mercury being used. The charge was made up as follows:—

88	parts	of roasted matte
9	„	quartz or quartzose ores
3	„	liquation residues
20	„	lead-bearing additions (litharge, hearths, residues from the zinc desilvering process, and *abstrich*)
5	„	limestone,

the amounts being so proportioned that 600 units of lead were present for every unit of auriferous silver, and 1·8 to 1·9 tons of charge were worked off in 12 hours with a consumption of 156 cubic feet of charcoal for every 10 tons of ore. The products were rich lead with 0·2 to 0·29 per cent. of auriferous silver, and a second matte ("*zweiten Verbleiungs-stein*") containing 0·04 to 0·05 per cent. of silver, 5 to 6 per cent. of lead, and 5 to 6 per cent. of copper, the slag produced being added to the first ore smelting charge.

This second matte is then leaded or desilverised again, being twice roasted and then smelted in similar furnaces to those employed in the preceding operation, 600 parts of lead being present in the charge for every one part of silver. Copper ores are also added to the extent of three per cent., with the object of producing a richer copper matte, and 1·2 to 1·3 tons of charge are smelted in twelve hours, the blast pressure being 0·47 to 0·62 inches of mercury, and 805 to 840 cubic feet of charcoal being required for every ten tons of matte.

The products are work lead with 15 per cent. of silver and a

"first desilverising matte" (*Ersten Entsilberungsstein*) with 0·018 to 0·02 per cent. of auriferous silver, 4 per cent. of lead, and 16 to 17 per cent. of copper. The slag produced is thrown away. The matte is then submitted to still another leading operation, being twice roasted and then smelted as before, but this time 1,500 to 1,600 parts of lead are present in the charge for every unit of auriferous silver. In twelve hours 1 to 1·2 tons of charge are smelted, with a consumption of 875 cubic feet of charcoal for each ten tons, and the products are work-lead with 0·05 to 0·08 per cent. of silver and copper matte, with 30 to 40 per cent. of copper and 2 to 3 per cent. of lead. This matte is then roasted and smelted, producing black copper with 0·008 to 0·01 per cent. of silver, which is afterwards refined.

At the works at Kapnik the matte containing 0·04 to 0·05 per cent. of auriferous silver and 12 per cent. of lead, in addition to a small amount of copper, is roasted three times and then smelted in blast furnaces with quartzose silver ores and lead-containing materials (litharge, old hearths, liquation residues, and residues from the zinc desilverising process), the amount being so adjusted that 500 parts of lead are present for each part of silver. The products are work-lead with 0·15 to 0·17 per cent. of auriferous silver, and matte with 0·04 per cent. of silver. The matte is roasted three times, and smelted as before, 750 parts of lead being present in the charge for one of silver, and the matte obtained again undergoes the same operations, 1,350 parts of lead being now added in the smelting process for each unit of silver. In this way work-lead and matte are produced, and the latter is then worked up for blister copper, which is refined at Felsöbanya.

At the works at Zalathna, in Transylvania, a portion of the matte is freed as far as possible from iron sulphide by treatment with dilute sulphuric acid before being leaded, another portion being roasted four times in heaps before the leading operation. The portion to be treated with sulphuric acid is first broken up with a rock crusher, and then powdered in a ball-mill. The sulphuric acid employed has a strength of only 22° Beaumé. Square leaden tanks, three feet long and broad and four feet high, are used for the treatment with sulphuric acid, and they are provided with copper exit pipes. Each tank is surrounded with a wooden jacket, and into the space between the jacket and the tank, steam at half an atmosphere pressure is admitted so as to hasten the reaction. Two leaden pipes with hydraulic lutes pass through the cover and dip into the liquid, and they serve for the introduction of the powdered matte. The sulphuretted hydrogen

produced is passed into a precipitating tower, where sulphur is obtained from it by the action of sulphurous acid.[1]

The powdered matte is introduced into the tank in quantities of 2 to 3½ lbs. until the entire charge of 3 cwts. has been added, this requiring 12 hours. At the conclusion of this time the mass is stirred for 6 hours and then allowed a further period of 6 hours for settling, after which the liquid and the matte are withdrawn through separate openings. The entire operation from the introduction of the charge lasts 30 hours, about 4 cwt. of matte being passed through the set of 6 tanks every 12 hours. Each cwt. of matte requires about a cwt. and a half of sulphuric acid of 50° B, and every 100 parts of matte leave 34 parts by weight of residue.

The sulphuric acid decomposes part of the iron sulphide in the matte, ferrous sulphate going into solution and sulphuretted hydrogen being evolved. Copper sulphide is not attacked by the dilute acid and remains behind, together with the precious metals, in the residue which is deprived of the greater part of its water by passing through a filter tank.

By this treatment the iron sulphide in the matte can only be reduced to a certain extent and the residue contains considerable quantities of basic salts which are only imperfectly removed by washing and interfere with the subsequent operation of leading.

The residue has the following composition:—

Iron	42·57	Arsenic . . .	traces
Copper	2·75	Sulphur	8·85
Lead.	6·04	Sulphuric acid . .	30.04
Silver	0·101	Oxygen	6·0
Gold	0·038	Slag	4·20

This process of treating the matte before leading can only be carried on in exceptional cases, as for instance where sulphuric acid is cheap and where sulphur and ferrous sulphate both command high prices.

The residue from the extraction, together with the matte which has been roasted in heaps, is smelted in blast furnaces with materials rich in lead. Owing to the large percentage of sulphur in the matte, the formation of a fresh matte in the smelting operation cannot be avoided, and this retains a certain quantity of the precious metals. The charge also contains rich raw ores, and a proportionately large amount of roasted pyritic slimes. The latter, which still contain 6 per cent. of sulphur, are requisite for the success of the smelting

[1] Schnabel, Mittheilungen über österreichisch-ungarische Metallhütten," *Minist.-Zeitschr. für das Berg-, Hütten- und Salinenwesen*, XXXVI.

operation, which could not be carried on with the matte residues alone on account of the large amount of basic salts that they contain.

The materials for furnishing the requisite lead are litharge and old cupellation hearths, the amount being so adjusted that 240 parts of lead are present for every unit of auriferous silver that has to be leaded. In the year 1887 the charge was made up as follows:—

32	parts of	slag
23	„	roasted pyrites
6 to 7	„	raw quartzose telluride ores
5·4	„	raw rich pyrites
9	„	matte residues
7	„	heap-roasted matte
10	„	materials containing lead.

The blast furnaces used are about 20 feet high, of circular section, 39 inches diameter at the throat, and 35½ inches at the tuyere level; they are arranged as sump furnaces, have two tuyeres, and are worked with a blast pressure of ⅜ of an inch of mercury. In twenty-four hours 1·95 tons of charge are worked off in addition to a ton of slag, 7 cubic feet of charcoal being burnt for every cwt. of charge. The products consist of:—

5·88	per cent.	of	work-lead
25·57	„	„	matte
68·55	„	„	slag

and the work-lead has the following composition:—

Lead	99·346	Silver	0·326
Antimony	0·018	Gold	0·310
Copper	traces	Iron	traces

The matte contains:—

Iron	66·33	Gold	0·005
Copper	1·18	Sulphur	25·98
Lead	5·65	Slag	0·78
Silver	0·071		

The silver is taken up by the matte to a considerably greater extent than the gold. In the first matte from ore smelting the amount of

gold is only about half that of the silver, whilst in the matte from the leading operation it does not amount to the tenth part of the silver content. The composition of the slag is :—

Silica	36·65	Alumina	1·30
Ferrous oxide	48·10	Lead oxide	5·22
Manganous oxide	1·75	Sulphur	0·54
Lime	6·44	Silver	0·0024
		Gold	0·0004

It lies between a mono- and a bi-silicate.

The matte from the leading operation is treated with dilute sulphuric acid in the same way as matte from the ore smelting, and the residue is leaded in the same way as the residue from the first matte extraction. In this second leading, a matte considerably richer in copper is produced, which is treated just as before, and when its copper content attains to 30 per cent. it is sent to the copper works.

At the Rothenbacher works, at Müsen, near Siegen, the mattes are leaded in the following way :—

The cupriferous lead matte from the smelting of lead ore and fahl ore is twice roasted in heaps and then smelted in blast furnaces, yielding a work-lead with 0·34 to 0·40 per cent. of silver, and a second lead matte with 20 to 25 per cent. of lead, 15 per cent. of copper, and 0·18 per cent. of silver. This second matte is twice roasted in heaps and again smelted in a blast furnace, yielding a third lead matte with 18 to 20 per cent. of lead, 30 to 40 per cent. of copper, and 0·17 per cent. of silver and a work-lead with 0·35 to 0·40 per cent. of silver. The third matte again undergoes the same series of operations, yielding work-lead with 0·35 per cent. of silver and a fourth lead matte or copper matte with 10 to 12 per cent. of lead, 45 to 55 per cent. of copper, and 0·17 per cent. of silver. The copper matte is smelted three times in a blast furnace with litharge and old cupellation hearths, and the thrice desilverised matte is now roasted and again smelted with litharge and old hearths. In this way a work-lead with 0·14 to 0·15 per cent. of silver, and lastly, a copper matte with 0·01 per cent. of silver are obtained, the latter being worked up for blister copper and refined copper.

The methods used in working the mattes at Freiberg and in the upper Harz have already been described under the roasting and reduction process and the iron-reduction process of lead smelting respectively.

Desilverising Mattes by means of Lead and Copper Conjointly

(*"Kupferauflösungsschmelzen und Abdarrprozess"*)

Under this head come the above two old processes for desilverising argentiferous mattes, neither of which are now in use. In both methods the desilverising is not effected by lead alone, but partly with the aid of copper.

In the first, or "copper-dissolving and smelting" process, the roasted argentiferous copper matte is smelted together with black copper and litharge in blast furnaces. The copper is converted into matte, taking the place of part of the silver which is taken up by the lead formed by the reduction of the litharge. The products are work-lead and plumbiferous copper matte, and the latter is smelted in the raw state with the addition of slags containing lead and with metallic iron in blast furnaces, yielding copper matte, which is further desilverised with lead and then worked up for copper. This process was formerly in use at Fernezely in Hungary.[1]

In the "drying-up" process (*Abdarrprozess*) the copper-lead matte from the smelting of copper and silver ores is smelted in low blast furnaces (*krummöfen*), together with black copper or residues from the liquation furnace and lead ores or materials rich in lead. The products are an argentiferous copper-lead alloy (liquation cakes) and a matte poor in silver. The latter is treated again in a similar way and the alloy is liquated, giving work-lead and liquation residues (*kienstöcke*) of copper containing a good deal of lead. The residues are used instead of black copper in the first operation for desilverising a further quantity of matte. By repeating these operations several times, work-lead containing most of the silver and desilverised copper are obtained.

This process, which is only applicable to argentiferous copper mattes or to argentiferous copper ores, is a combination of the liquation process with the leading and smelting operation. It furnishes a more complete desilverisation than the liquation process, and yields also a purer copper, but it is both complicated and costly.

Both the above processes have only been used in Hungary and in the Tyrol, and both of them have long since been abandoned on account of their costliness and tediousness.

b. Production of Work-Lead from Speiss

Argentiferous speiss can be desilverised either by mixing it with molten lead or by smelting it with materials rich in that metal. It

[1] Karsten, *System der Metallurgie*, vol. 5, p. 563.

must be thoroughly roasted before leading in order to free it as far as possible from arsenic and antimony.

The products are work-lead and a speiss poorer in silver. In order to transfer the copper content and a portion of the silver into a matte, pyrites is added in the smelting operation, and in order to concentrate the nickel and cobalt the speiss is repeatedly smelted, after previously roasting each time, with pyrites or copper matte.

Davies[1] treats the molten speiss in quantities of half a ton with 20 to 25 per cent. of lead in a converter of iron plate lined with fire brick, having the form of a horizonal cylinder. Air at a pressure of 17 ounces is forced through the mass for three or four minutes by a pipe $\frac{1}{4}$ of an inch in diameter, in order to bring the lead into intimate contact with the speiss and to volatilise a portion of the arsenic of the latter. The converter is then turned round, the molten contents running out into a slag pot; the desilverised speiss which floats on the lead is removed in crusts from its surface, and the lead run off afterwards. This process is said to have given favourable results at the Eureka Consolidated works, Nevada, though the author is doubtful as to the economical success of the process, as considerable quantities of lead must be oxidised by the blast and the oxide fluxed by the lining. The leading of a speiss is an imperfect operation which has generally been replaced by wet methods of desilverising.

c. The Desilverisation of Alloys by means of Lead

The only alloys which are desilverised in this way are those of copper and silver, which form argentiferous black copper or blister copper.

The leading of these copper-silver alloys can either be carried out by means of a bath of molten lead or by liquation.

The first process is a very imperfect one and has been entirely superseded by wet methods of desilverising. Argentiferous copper coins have been desilverised in the lead bath of the cupellation furnace, but copper goes into the litharge and has to be recovered from it by reduction, whilst the method is attended with a large loss of copper and silver, and is no longer used.

The liquation method is also an antiquated process, which was, however, formerly in very general use for extracting silver from copper-silver alloys and it will for that reason now be described in detail.

[1] *Engineering and Mining Journal*, June 30, 1888.

The Liquation Process for Desilverising Copper-silver Alloys

When argentiferous copper is melted together with lead, a lead-copper-silver alloy is produced. If the lead in this alloy bears a proper proportion to the amount of copper present, it is possible by heating the solid alloy to a certain temperature, to obtain the greater portion of the silver alloyed with lead flowing away in the liquid state, leaving the copper behind in the solid residue. A portion of the silver and of the lead are left in the copper, and some copper finds its way into the lead-silver alloy.

By again heating the alloy in presence of air, the greater part of the silver remaining behind can be obtained in combination with lead lead oxide and cuprous oxide.

This is the basis of the liquation process which was formerly in very general use, but which is not worked now at all on account of certain drawbacks inherent to it. These disadvantages are the large losses of lead, silver (21 per cent.) and of copper taking place in the process, and the expense due to the number of operations which the bye-products have to undergo.

The various operations were as follows:—

1. The production of the lead-copper-silver alloy or the "*frischen*," which was effected by melting the argentiferous copper with lead in a blast furnace.

2. The separation of this alloy into argentiferous lead and a copper-lead-silver alloy poor in lead and silver. This was the *liquation* process (*Saigern*), and consisted in the liquation of the argentiferous lead from the alloy in a liquation hearth.

3. The separation of the remainder of the lead and silver from the alloy or the *drying* (*Darren*) process. This consisted of a further liquation of the argentiferous lead from the alloy, and an oxidation of the copper and lead by heating the liquation residue in a furnace (*drying* furnace) in an oxidising atmosphere.

The refining of the residue from the *drying* operation, and the working up of the intermediate products, have also to be taken into account.

1. *The "Freshening" or Leading of the Argentiferous Copper*

The copper which has to be leaded should be either in small pieces, obtained by breaking up the cakes of copper whilst hot, or else granulated.

Small blast furnaces (*krummöfen*), arranged as *spuröfen* where the liquid products at once flow out of the furnace, are employed for this

operation. The lead is added either in the metallic state or in the form of litharge, which is reduced to metal in the furnace. Experience has shown that not more than eleven parts of lead should be combined with three of copper, as otherwise too much copper goes into the work-lead in the liquation; and on the other hand there must be not less than 500 parts of lead for every one part of silver present, otherwise too much silver is left behind in the copper. If the copper is so poor in silver that the addition of lead in the requisite proportion disturbs the proper ratio between the lead and copper, then liquated work-lead can be used in order to keep these proportions constant. If the silver content of the copper amounts to more than 0·6 per cent., the liquation process must be repeated, and in this way a poorer argentiferous lead is obtained which can, however, be used for desilverising fresh quantities of copper.

The proportion of 3 of copper to 11 of lead corresponds nearly to the formula CuPb, which would require 3 : 9·8.

Owing to the necessity of maintaining the lead and copper in these proportions, only so much lead and copper are melted together in the furnace at one time as are required to form a single liquation cake 3 to 3½ inches thick.

At first, a mixture of fuel and some slag is put into the furnace, and as soon as the molten slag appears, sufficient raw copper for the first liquation cake is added. When this is red hot, which takes four or five minutes, the previously weighed quantity of lead is added. As soon as the molten alloy produced has collected in the forehearth, where it is covered with slag, a further weighed amount of copper is put into the furnace to be followed by a further weighed quantity of lead. In successful work a fresh liquation cake is made every 7 or 8 minutes. Slags with 40 to 60 per cent. of lead and 3 to 5 per cent. of copper are obtained in addition.

When litharge is employed instead of lead, the operation must be conducted more slowly to allow of the reduction of the litharge, otherwise too much and too rich a slag will be formed.

2. *The Liquation Process*

This operation is carried out in absence of air, as otherwise the lead separating in the fluid state from the alloy would be converted into litharge. It cannot be satisfactorily performed in a reverberatory furnace, and a special form of liquation furnace (*Saigerheerd*) was consequently devised.

This furnace, shown in Fig. 306, consists of two brick walls *S*, each 6 feet long and 2 feet high sloping towards each other, and a back wall *b* with a short vertical chimney. The brick walls (*Saiger-*

bänke) are covered on their sloping tops with cast-iron plates *c, c* (*Saigerschwarten*), a small channel (*Saigerritze*) remaining between the lower edges of these plates. The space *d* between the two walls sloping from back to front is floored either with masonry or with cast-iron plates, and leads into a trough *p* in front.

The cakes or discs to be liquated are set up on edge on the plates *c* at a short distance frome one another, 6 to 8 discs being treated at once. The space between the discs is filled with charcoal, and charcoal is heaped over the discs, and iron plates with vent holes are then placed round the charcoal.

The charcoal is ignited by means of a wood fire made in the channel between the two walls, and as a result of the heating, which

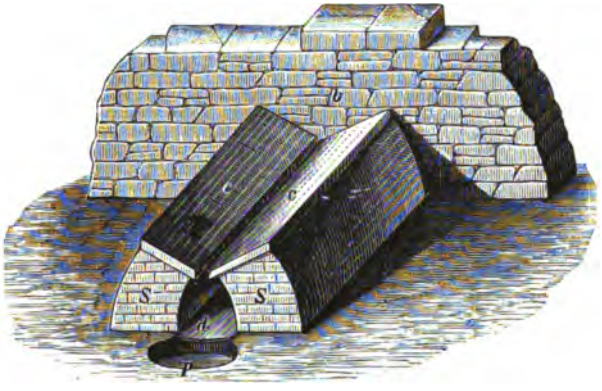


FIG. 306.

requires very careful regulation, the lead-silver alloy drains away from the cakes, runs through the space between the two plates, and flows down the channel *d* into the hearth *p*, leaving behind the copper as a solid residue.

The lead is known as liquated lead ("*saigerblei*"), and the residue as "*kienstöcke.*" As the access of air cannot be entirely prevented, a slag containing oxides of lead and copper is formed which is known as "*saigerkrätze,*" the quantity produced depending upon the temperature. When the lead ceases to flow out, the liquation is finished, and the charcoal is raked out from between the pieces of residue, which are then cooled by sprinkling water over them.

The liquated lead contains 2 to 3 per cent. of copper, whilst the residue retains 25 to 35 per cent. of lead, and in good working, 87 per cent. of the lead content of the cakes should be obtained in the liquated lead, 13 per cent. being left behind in the residue.

When the liquated lead is sufficiently rich in silver it is cupelled, otherwise it is used again in the process. The residue is submitted to the "drying" operation in order to further deprive it of lead and copper, whilst the *saigerkrätze* are either added to the leading operation in the first instance, or else they are made up into liquation cakes with other bye-products of the process.

3. *The "Drying" Process ("Darren")*

This is an extension of the liquation process, and aims at removing as much lead and silver as possible from the residue.

This could be effected by prolonging the liquation process, but as the liquation hearth is costly to work, the "drying" process is conducted in large reverberatory furnaces, which not only give a better return than the hearths, but are less costly, on account of the cheaper fuel which can be used.

In the reverberatory furnace air is not excluded, and consequently the lead is obtained mostly as oxide. This oxidation would, however, also take place in liquating the residues in hearths, because in order to liquate the residue a high temperature is necessary.

The "drying" furnace is a reverberatory having several parallel walls in the heating chamber ["drying benches" (*darrbänke*)], and between these walls are channels floored either with brasque or else with cast-iron plates, and sloping from back to front of the furnace. Each channel communicates by means of a flue at the back with the chimney, and the furnace is either fired in these channels or else by grates placed at each side of the furnace. The front of the heating chamber is closed by means of a door sliding in iron grooves, which can readily be raised or lowered.

The Figs. 307 and 308 show the construction of such a drying furnace provided with a grate at each side; *p*, *p*, are the two fireplaces, *b*, *b*, the channels, and *c* the floor of the channels between the walls *a*, *d* is the sliding door, and *h*, *h*, are the flues.

The pieces of residue to be liquated are laid on the benches, and the whole space up to the roof of the chamber is filled with these pieces, so placed as not to prevent the circulation of the hot air round them. The sliding door is now closed, and a wood fire, gradually increasing in intensity, is started on the grates or in the spaces between the walls. At first lead alone flows away, but soon a mixture of cuprous and lead oxides ("*darrost*") drops down into the channels, where it solidifies, and from which it is raked away.

This "drying" process, like the operation of liquation, is based

upon the fact that lead having a lower melting point than copper will flow away from the surface of the cakes either as metal or as oxide. The lead remaining, according to Karsten, then equilibrates itself with the whole mass of the remaining copper, until the equilibrium

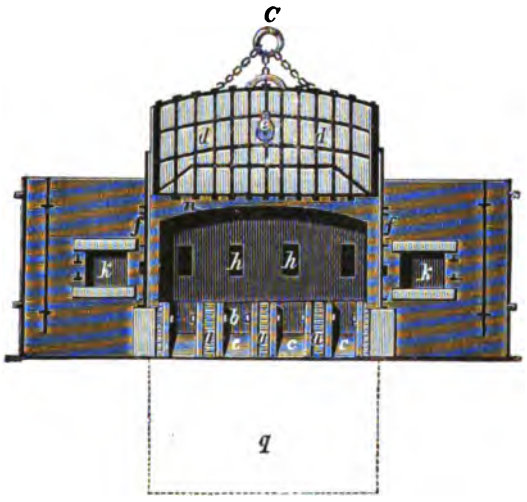


Fig. 307.

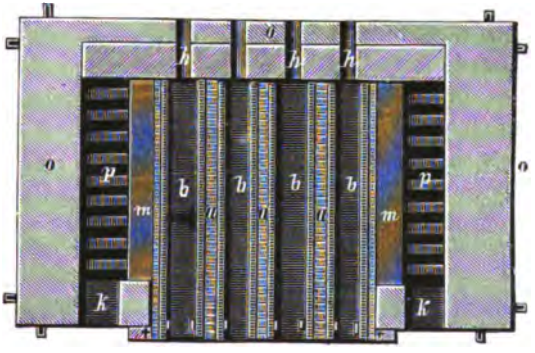


Fig. 308.

is disturbed by more lead draining away, and so the operation goes on.

The "*darrost*" contains 75 to 85 per cent. of lead oxide, and 4 to 8 per cent. of cuprous oxide, besides variable quantities of silica and alumina from the masonry of the floor and walls of the furnace. The residues remaining behind are called "*darrlinge*," and at the conclusion of the operation (which lasts about 24 hours) they are drawn

red-hot from the furnace and thrown into a well or sump containing water.

After cooling, the rind or crust which has not already broken in the quick cooling, is broken up by pointed hammers. This crust is a mixture of argentiferous lead and copper oxides, and is called "*pickschiefer*." Both the *darrost* and the *pickschiefer* are smelted in low blast furnaces for work-lead.

The *darrlinge* still contain on an average 15 per cent. of lead, and are refined, the greater part of the lead volatilising during the operation.

The process of liquation has, on account of the losses of metal attendant on it and on account of the lengthy operations involved, been generally superseded by wet processes or electrolytic methods.

d. The Production of Work-Lead from other Metallurgical Products

The remaining metallurgical products, which are desilverised by converting their silver content into a lead-silver alloy or work-lead, are: cupriferous and argentiferous scrapings or scums (*Krätzen, schlicker*), rich oxides from the zinc desilverising process, litharge rich in silver, old cupellation hearths, and the *abstriche* and scums formed in refining lead, argentiferous flue dust, slags and various argentiferous bye-products obtained in wet or electrolytic processes, such as argentiferous slimes from the sulphuric acid liquors, silver sulphide, and anode slimes.

All of these intermediate products, with the exception of those which are rich in silver, are worked up with argentiferous lead ores or mattes, or with silver ores. Those which are rich in silver are treated directly in a bath of molten lead, and in all cases the methods of working are precisely similar to those which have been previously described.

THE CONCENTRATION OF THE SILVER IN WORK-LEAD

The concentration of silver in poor silver lead is effected either by a partial cupellation, Pattinson's process, or else by means of the zinc process.

Either of the two latter methods may be used for enriching work-lead before cupellation. In both these methods the lead is obtained as market lead, together with a much smaller amount of a rich silver-lead alloy or a silver-zinc-lead alloy.

As to whether a particular silver-lead alloy can be economically cupelled directly, depends upon local conditions and upon the price

of silver; but speaking generally, it may be said that lead containing less than 0·12 per cent. of silver cannot be economically cupelled. In special cases it is advisable to enrich even rich silver-lead, as in both concentration processes market lead is obtained directly, whilst by cupellation the whole of the lead is converted into litharge, the reduction of which is attended by considerable loss of lead.

The Pattinson process in which the work-lead, by slow cooling from the molten state, is separated into crystals poor in silver and a fluid portion rich in silver, is only applicable to the production of an alloy containing, at the most, 2½ per cent. of silver.

In the zinc process the silver is separated from the work-lead in the form of a silver-zinc-lead alloy, the lead poor in silver remaining behind. The triple alloy yields after separating the zinc a lead-silver alloy, which may attain to a much higher silver content than the rich alloy obtained in the Pattinson process.

The zinc process produces market lead in a much shorter time and in a much purer condition than the Pattinson process, gives a more thorough extraction of the silver, and yields an alloy much richer in silver than the latter process, besides being less costly. Consequently the zinc process is the more extensively employed, Pattinson's process only being used under particular local conditions. This rule only holds, of course, as long as the price of zinc remains within reasonable limits, and if these should be exceeded, the Pattinson process could be worked at an advantage as compared with the other.

The Pattinson Process

This method of desilverising lead is based on the observation of Pattinson in 1833, that if molten argentiferous lead be slowly cooled the portions solidifying first are crystalline, and much poorer in silver than the still liquid portions. If the liquid richer portion be separated, it again can be divided into a poorer solid portion and a still richer liquid alloy, and this operation can be repeated until the enriched lead contains 2·5 per cent. of silver. After this point no further separation is possible, as the crystals and the liquid portion will have almost the same silver content.

Similarly the solid crystalline portions poorer in silver may be treated again, and the molten metal be split into crystals poorer and a fluid portion richer in silver, until by repetition of the operation lead very low in silver is produced; for economic reasons the desilverisation of the lead crystals is not carried below 0·001 per cent. of silver.

By means of this Pattinson process, the theory of which has never been satisfactorily explained, work-lead can thus be separated into enriched lead containing up to 2·5 per cent., and market lead holding only 0·001 per cent. of silver.

The limiting silver content at which work-lead may still be desilverised with advantage by this process depends upon local conditions, but is generally taken as about 0·009 per cent. of silver.

The process demands a pure lead and the careful regulation of the temperature of the metal. Impurities in the lead, such as copper, nickel, arsenic and antimony, hinder the separation of the crystals and the mother liquor, and thus render the desilverising imperfect; copper distributes itself between the crystalline and the fluid portions; arsenic goes chiefly into the solid crystalline portions, and antimony and nickel into the liquid alloy.

Impure lead must consequently be refined before being submitted to Pattinson's process, and, if the percentage of copper be high, must even be liquated before refining. This operation has already been described (*see* Lead, pages 430 and 443).

When the amount of copper is smaller it separates on the surface of the lead when melted, in the form of a lead-copper alloy or scum (*schlicker*). Small quantities of arsenic and antimony can be got rid of by poling as they pass into the dross produced.

In order to obtain the requisite temperature, considerable quantities of lead must be melted, as otherwise the temperature cannot be perfectly controlled. At too high a temperature no crystals are formed, and, if the temperature falls too low, it is impossible to separate the crystals from the liquid. From 10 to 20 tons of work-lead are accordingly melted at one time in cast iron vessels.

In actual practice there are two systems, according to which the crystals are separated from the mother liquor, as the fluid portion is called. In the system of thirds, $\frac{2}{3}$ of the volume of the molten lead are separated as crystals and $\frac{1}{3}$ left as mother liquor; whilst in the system of eighths, $\frac{7}{8}$ of the lead are separated as crystals and $\frac{1}{8}$ left as mother liquor.

When the system of thirds is employed then each operation practically doubles the silver percentage, whereas the system of eighths trebles it. Consequently the first method is used for lead rich in silver, and the latter, the system of eighths, for poor silver-lead.

Other methods are also used, such as combinations of the above two systems, and the system of thirds with intermediate crystals. In this latter system, the contents of the pot are divided into more than

two portions, usually into three, viz., poor crystals, richer intermediate crystals, and mother liquor, and these three portions are then worked up separately.

The Pattinson process is conducted in large pots of cast-iron or cast-steel. The crystals are separated from the mother liquor either by ladling them out from the pot or else by tapping off the mother liquor and leaving the crystals behind, and the formation and separation of the crystals is effected either by stirring the cooling mass or by blowing steam through it.

There are then two ways of conducting the operation :—

I. Hand-pattinsonising, where the crystals are ladled out and the liquor left behind.

II. The tapping process, steam-pattinsonising or Rozan process, where the fluid portion is tapped off, leaving the crystals behind.

The cost of the first process is higher than that of the second, and on that account its employment at the present day is exceptional.

I. The Hand-Pattinsonising Process

This method is carried out in semicircular pots of cast-iron. They are generally between 5 and 7 feet diameter, and from 35 to 37 inches deep, 1¼ to 3 inches thick at the bottom, and 1 to 2 inches at the top, and hold 10 to 15 tons of lead. They are usually supported by means of a projecting ring on their upper outer edges, which rests upon an iron ring supported by the masonry of the setting.

The arrangement of a series of such vessels, each holding 12·5 tons of lead, formerly in use at the Lautenthal works in the Harz, or hand-pattinsonising, is shown in Figs. 309 to 311; *K K* are the pots and *A A* the fireplaces of each. The flame from the coal used as fuel strikes the bottom of the pot first, passes through an opening *o* in the circular brickwork support *m*, into the annular flue *v*, and passing round the pot reaches the flue *y* and passes through it and *z* away to the chimney.

Up to as many as 24 pots may be set in a series or *battery*, according to the method of conducting the process.

The lead is first melted in the pot and any scum or dross (*schlicker*) forming on the surface is skimmed off and, if necessary, a further purification by poling is resorted to. When the lead is freed from impurities the fire in the grate is withdrawn or generally transferred to the grate of the adjoining pot, and the surface of the molten metal is carefully sprinkled with water. In consequence of the slow cooling which ensues, crusts form upon the surface and sides of the bath of metal and these are thrust down and mixed up with the rest of the

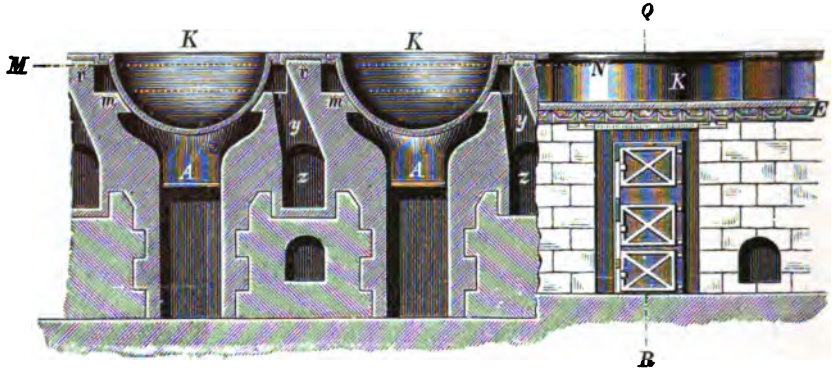


Fig. 309.

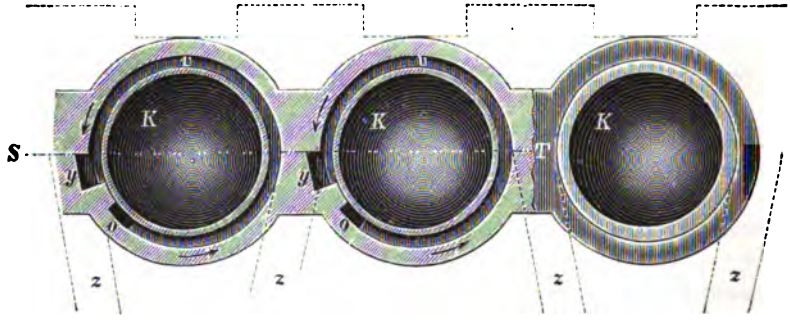


Fig. 310.

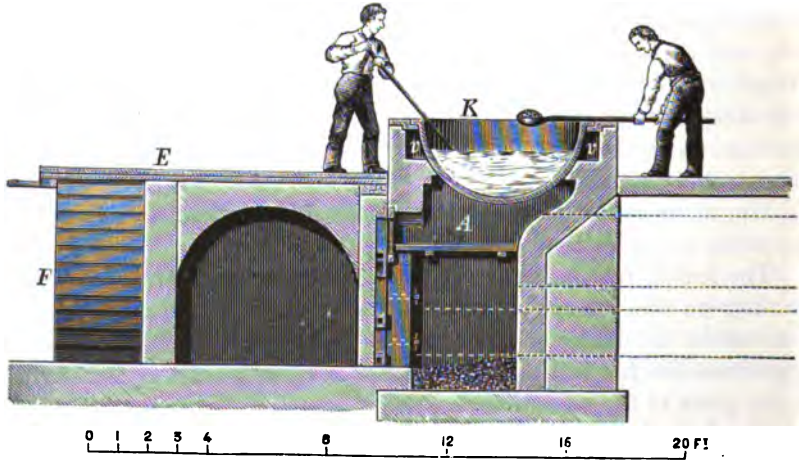


Fig. 311.

metal in order to ensure a uniform reduction of temperature. As soon as the surface of the bath becomes uneven and the metal is of an almost semi-pasty consistency, crystallisation is sufficiently advanced, and the work of ladling out the crystals begins.

This is effected by two or four workmen working at one or on the two opposite sides of the pot with perforated ladles, and either $\frac{2}{3}$ or $\frac{7}{8}$ of the contents of the pot are removed as crystals, according to whether the thirds or eighths system of working is in use. The volume of the crystals ladled out is measured by means of a right-angled measure laid across the top of the pot.

The enriched third or eighth of the original lead is either ladled out of the pot into an adjoining one in the system of thirds, or else, if the method of eighths is in use, it is, if necessary, cast into moulds.

The crystals obtained in this way are small elongated octahedra with raised edges which, as they only grow in one direction, appear as long four-sided pyramids.

To the crystals which have been ladled over, a quantity of lead of the same silver content is now added, so that the pot again contains its normal quantity; that is to say, with the thirds system, $\frac{1}{3}$ of the normal contents of the pot must be added, and $\frac{1}{8}$ with the eighths system. To the mother liquor remaining behind, either $\frac{2}{3}$ or $\frac{7}{8}$ of the volume of the pot, of lead of the same silver content as the mother liquor must be added. Then in both cases the operation of desilverising is repeated just as in the case of the pot full of the original lead.

In the ordinary working of the thirds system, the entire quantity of argentiferous lead is in the pots, of which there may be 15.

If lead of varying percentages of silver is available, then it is easy to keep the pots full, otherwise the battery must be kept at its normal point by crystallising various sorts of lead until alloys of lead and silver of the correct percentage are obtained. In regular working, lead of a certain silver content is put into the charging pot, and at one end of the battery poor lead is obtained, and at the other a rich silver-lead of definite composition.

In the system of eighths, from 2 to 6 pots are worked together, but the process does not go on uninterruptedly as in the thirds system until lead of the requisite silver content is produced, it being necessary from time to time to bring the requisite material of proper silver content from the so-called "reserves." If the requisite quantity of reserves is obtainable, then it is possible to continue for a time working for rich and poor lead, when the production of reserves has again to be taken in hand.

The system of eighths, though requiring fewer pots and yielding

rich lead more quickly than the thirds system, still has the disadvantage that certain portions of the lead obtained by the various meltings —viz., those of medium silver content—cannot be worked up at once, but must wait until the requisite amount to fill a pot has been accumulated.

In order to illustrate the working of the thirds system the treatment of Freiberg *"freshened"* lead with 0·02 per cent. of silver by means of the hand-pattinsonising process, will now be considered, a battery of 14 pots being employed.

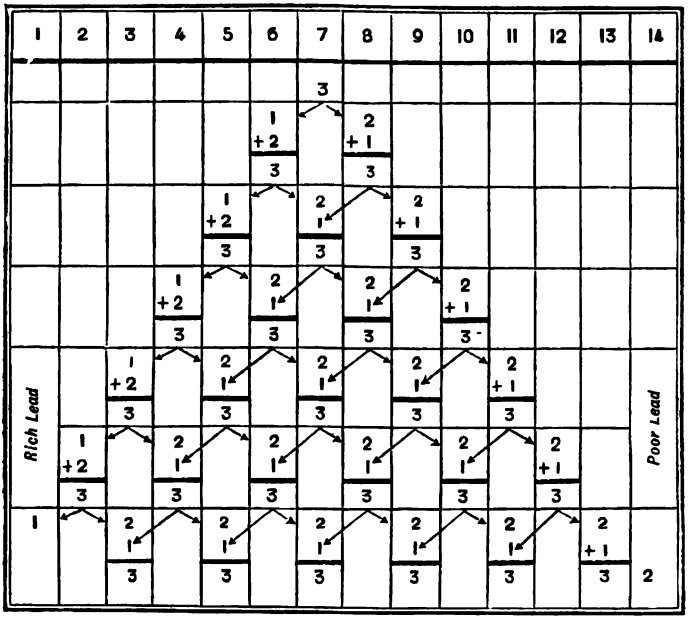
It is assumed that lead with the requisite percentage of silver is available to keep the pots filled to their working level. In the diagram the number 3 signifies a pot entirely full, equal to 10 tons of lead, 2 means that the pot is $\frac{2}{3}$ full, and 1 that the pot is one third full. The numbers 1 to 14 at the top of the diagram indicate the numbers of the various pots, and the sign + signifies the lead added from the stock.

The work lead with 0·02 per cent. of silver is charged in the seventh pot, and after it is melted and cooled, $\frac{2}{3}$ of its contents are ladled out in the form of crystals and put into pot 8, the remaining liquid $\frac{1}{3}$ being put into pot No. 6. In order that a fresh crystallisation can be effected in pots 6 and 8, they have added to them $\frac{2}{3}$ and $\frac{1}{3}$ respectively of their contents of lead of the same percentage of silver as each of them contain, from the stock of reserves. The contents of both of these pots are now melted and allowed to begin to crystallise, and then $\frac{2}{3}$ of the contents of pot No. 6. = 6·5 tons of crystals, are ladled out into pot No. 7, and the remaining third or 3·5 tons of mother liquor is put into pot No. 5; from the eighth pot 6·5 tons of crystals are ladled into pot No. 9, and 3·5 tons of mother liquor go to pot No. 7. Pot No. 7 has in this way received another full charge, whilst pots Nos. 5 and 9 are made up to the requisite quantity by the addition of 6·5 and 3·5 tons of lead of corresponding silver content. The pots Nos. 5, 7, and 9 can now be crystallised, and after those, pots 4, 6, 8 and 10, and by continuing the working in this way, poor lead is at last obtained with 0·002 per cent. of silver and rich lead with at least 1·5 per cent. of silver.[1] At Freiberg, at present, the lead is only desilverised down to 0·1 per cent. of silver, and is then submitted to the zinc desilverising process.

As will be gathered from the above scheme, the pots with even and uneven numbers are worked alternately. There are, however, considerable deviations from the above method in practice, as regards the choice of the charging pot, the number of crystallisations, and the

[1] *Plattner-Richter's Vorlesungen*, 2. p. 248.

number of pots that are worked simultaneously. The position of the charging pot and the number of crystallisations that are necessary depends upon the amount of silver in the lead. In the case of rich silver-lead the work-lead is put into the third or fourth pot counting from the left end of the series, so that the rich lead is obtained with a smaller number of crystallisations and ladlings to the left. A greater number of crystallisations are, however, necessary in order to obtain the poor lead which has to travel further to the right. On the contrary, with lead poor in silver, the market lead is obtained more quickly. The whole of the evenly or unevenly numbered pots of a battery are not usually being worked at the same time, as the amount



of work-lead requisite for this is often not available, whilst the number of workmen required would be considerable. Usually crystallisation is only being carried out in a limited number of pots, and when they are worked off, the operation is continued in a similar number of the other pots of the series which have received a full charge of metal.

In order to properly control the process, the percentage of silver present in the charges in the various pots must be ascertained from time to time, and if it is found that the percentage is decreasing irregularly towards the market pot, then the contents of each pot

from that up to at least the charging pot must be ladled back into the adjoining one before crystallisation is begun again.

For economic reasons, as before stated, the lead is not worked to below 0·002 per cent of silver, except when assay lead is being made, which is done in a battery of 24 pots. In working the eighths system a battery of from 2 to 6 pots is used, usually only 2, and several batteries are worked simultaneously, so that sufficient lead of a proper silver content is always available for keeping the pots properly filled.

In working a battery of 2 pots, after the lead is melted, $\frac{7}{8}$ of the contents in the form of crystals are ladled over into the second pot, whilst the mother liquor is ladled into moulds. To the $\frac{7}{8}$ of crystals, $\frac{1}{8}$ of lead of the same silver content is then added from the stock, and the whole melted and crystallised, $\frac{7}{8}$ being ladled back into the first pot in the form of crystals, and the remaining $\frac{1}{8}$ being cast into moulds as a reserve.

This process of ladling back the crystals and ladling out the mother liquor is repeated until the lead is sufficiently desilverised. The enriched lead in the reserves is brought up to the requisite silver content as soon as sufficient is obtained to properly fill a pot, and to the $\frac{7}{8}$ of crystals thus obtained, lead of the same silver content is again added from the stock.

In using this method it is necessary, in order to furnish the requisite amount of lead of the proper silver percentage, to carry on a corresponding number of crystallisations of the original work-lead.

At the Binsfeldhammer works, near Stolberg, work-lead containing 0·05 per cent. of silver was formerly worked up by this process into rich lead with 1 to 1·5 per cent. of silver, and poor lead with 0·001 per cent. of silver.

The products obtained in Pattinson's process are rich lead, poor lead, scums ("*schlicker*") and scrapings or dross ("*krätzen, bleidreck*"). The scums and argentiferous drosses are added to the ore and matte smelting charges; the scums are sometimes liquated, yielding argentiferous lead and a residue which is cupiferous, and is consequently either added to the matte smelting charge, or smelted with galena or pyrites for matte and work-lead.

The lead dross poor in silver is worked up by smelting it with lead ores poor in silver, or else with intermediate products poor in silver, such as litharge, or it is smelted by itself for market lead.

The working returns of the hand-pattinsonising process show considerable variations, depending upon the purity and the richness of the lead as well as upon the calorific value of the fuel used.

For instance, at the Friedrichshütte, near Tarnowitz, where work-lead with 0·094 to 0·125 per cent. of silver was formerly desilverised by the thirds system in a battery of 14 pots, a charge of 15 tons being put in the third or fourth pot, from every 100 parts of work-lead, 84·21 parts of poor lead with 0·001 per cent. of silver, and 12·62 parts of rich lead, with 0·88 per cent. of silver, were obtained. The loss of lead was 3·17 per cent. The silver obtained exceeded that indicated by the assay (which however gave a result 2·5 per cent. too low) by 0·019 per cent. The fuel used was 0·811 tons of small coal and 60 cubic feet of *cinder* for every 5 tons of work-lead.[1]

In the Upper Harz working the thirds system on work-lead, averaging 0·14 per cent. of silver with charges of 12·5 tons in the third pot of a battery of 13, rich lead with 0·7 to 0·8 per cent. of silver was obtained, and poor lead with 0·001 per cent. of silver. At the Lautenthal works, according to Strauch, 118 logs of wood and 1·365 tons of coal were burnt for every 5 tons of lead pattinsonised.

According to Gruner, the loss of lead in the process amounts to 2 per cent., or, including that incurred during the preliminary refining, 3 to 6 per cent.; and the same authority gives the fuel consumption as 20 to 25 per cent. of the weight of the lead in coal and *cinder*.

At all the Continental works, with the exception of Freiberg, the the hand Pattinson process has been superseded by the method of desilverising with zinc. In the United States, where such great progress has recently been made in the working of argentiferous lead, the process has never come into use.

At Freiberg the Pattinson process is worked in conjunction with the zinc process, owing to the fact that the argentiferous lead contains bismuth. The pattinsonising of the lead down to 0·001 per cent. of silver is not however carried on now, the content of silver only being reduced to 0·1 per cent., and the further desilverising then effected by the zinc process.

The Tapping Process or the mechanical Pattinsonising, and the Rozan Processes

In these processes hand labour is to a great extent replaced by machinery, or the energy of the steam pressure is utilised directly. The melting and crystallising of the lead are not effected in the same vessel as in the process just described, but take place in separate vessels. Two processes come under this heading, differing

[1] Teichmann, *Preuss. Zeitschr.* 15, 44.

from one another in the manner in which the agitation of the molten mass is effected; they are:—

1. The mechanical Pattinson process, in which the stirring of the molten mass is effected by mechanical means, and—

2. The Rozan process, in which steam pressure is used for the agitation.

1. The Mechanical Pattinson Process

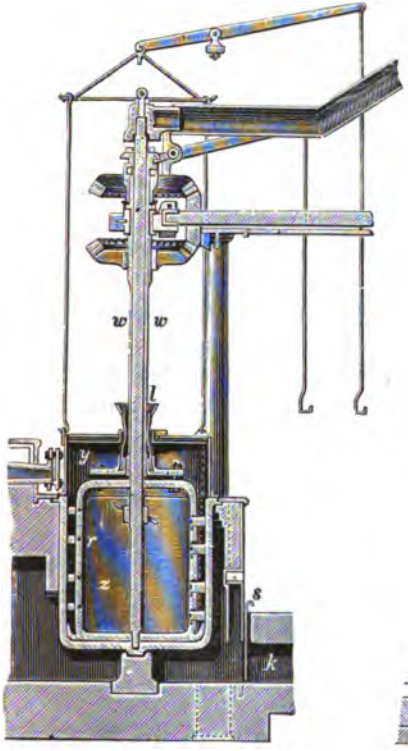
The manner of carrying out this process was suggested by Boudehen in the sixties, and it was first worked at Rouen and Stolberg.

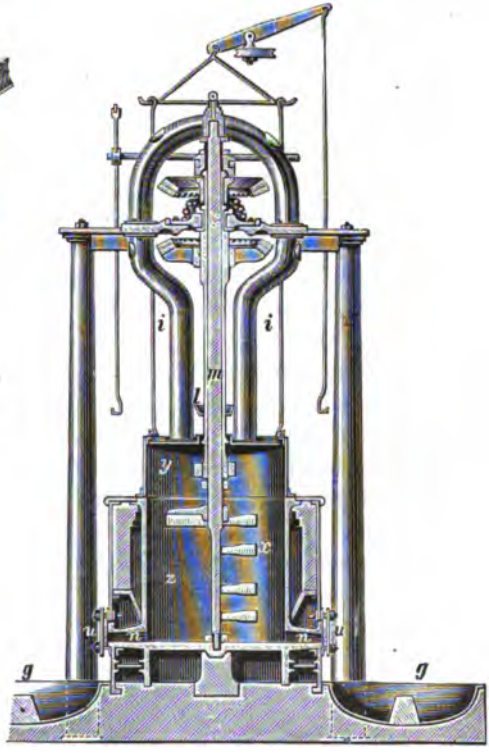
The arrangement adopted consists of one or two melting pots and a crystallising pot. The melting pot stands at a higher level than the crystallising pot, and only differs from the ordinary Pattinson pot in that it is provided with a valve at the lower part, through which the molten lead can be drawn off and run into the crystallising pot. If two melting vessels are used, then they are placed side by side on the same level.

The arrangement of the crystallising pot is shown in Figs. 312 and 313. It consists of a cast-iron cylinder *z*, about 4 feet high and 3 feet diameter, which can be heated by the waste heat from the melting pot. The gases enter through the flue *k*, provided with a damper *s*, and pass under the crystallising vessel, or if their heat is not required the damper is shut and the gases pass direct to the chimney. There are two stirrers in the cylinder, which rotate in opposite directions. One of them consists of a cast-iron framework *r*, provided with short arms and connected to the hollow axle *w*. The second stirrer, the axle of which passes through the hollow axle of the first, consists of a series of arms *x*, placed one above the other, reaching nearly to the rim of the first stirrer. Both stirrers can be rotated by the bevel wheels above. The cylinder is closed at its upper end by a movable cover *y*, and in this cover are the flue pipes *i*, *i*, for carrying off the lead fume. At the bottom of the cylinder are two outlet tubes *n*, *n*, provided with valves in order to allow the mother liquor or molten lead to be run off into the moulds *g*, *g*. From these moulds the blocks of lead (which have ringbolts cast into them) can be lifted by means of a crane after solidifying, and dropped by the same crane into the melting pot. The water necessary for cooling the molten lead at the commencement of crystallisation is introduced by means of the little trough *l* above the cylinder cover.

The working of the apparatus is carried out as follows :—

The lead is first melted in the melting pot, and is then allowed to run through the valve into the crystallising vessel previously heated by the waste heat from the melting pot. When the lead is introduced the damper is closed, and in order to cool the lead more quickly a certain amount of solid lead is thrown into the molten metal in the cylinder. Some pieces of coke are then thrown upon





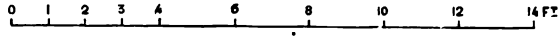


FIG. 312. FIG. 313.

the surface of the bath of metal, the stirrers are put in motion, and a small stream of water is allowed to flow in. As the bath becomes stiffer, owing to the separation of the crystals, more energy is necessary for the agitation of the mass. After stirring for an hour or an hour and a quarter with a charge of 10 tons of molten metal and 4 tons of solid lead, the lead is tapped off.

After running off the molten lead an equivalent quantity of lead

of the same silver content as the crystals, is run on to the remaining crystals. The crystals are melted by means of this molten addition without any further firing of the crystallising vessel. The stirrers are again set in motion, and allowed to run until the necessary amount of crystals has again been produced. The mother liquor is tapped off, more molten lead added to the crystals, and the process repeated until poor lead is ultimately obtained, the enriched lead being treated in the same way until mother liquor sufficiently rich in silver has been obtained.

It will be seen that in this process it is necessary to have in reserve a stock of lead containing varying percentages of silver, in order to add lead of the requisite richness to the crystals in the crystallising vessel. As a rule the system of thirds is the one employed, $\frac{1}{3}$ of the charge being run off as mother liquor, and $\frac{2}{3}$ left behind in the form of crystals.

According to Gruner, at Rouen, where the process was formerly in use, 10 to 12 crystallisations were made each day with charges of 9 and 12 tons of lead, using 8 to 12 horse-power for agitation. The work-lead contained 0·04 per cent. of silver. The coal used for melting amounted to 15 to 16 per cent. of the weight of the lead to be desilverised, and that required for the whole process, including the production of power, was equal to 25 per cent.

In Holzappel, where the process was also formerly used, rich lead with 2·4 per cent. of silver, and poor lead with 0·0036 per cent. were produced.

This process is considerably cheaper than hand-pattinsonising, but is more costly than the Rozan process, and much more costly than the zinc process, by which it has, in almost every instance, been replaced.

2. The Rozan Process

This process, known also as the Luce and Rozan process after its inventors, utilises steam pressure for the agitation of the molten lead. As the introduction of steam into the lead causes a large surface to be exposed to the air, the cooling of the mass is hastened, and at the same time various foreign bodies present, particularly copper, are separated out as the mass cools. Consequently, impure varieties of lead, which would require refining before being submitted to the ordinary Pattinson process, can be treated direct by the Rozan process. The lead most suitable for the process should not however contain more than $\frac{2}{3}$ per cent. of impurity; if more than this is present, a preliminary refining is advantageous.

The apparatus used for the process consists of one or two melting

pots placed side by side, and a crystallising vessel placed below them. Both have separate fireplaces, and the crystallising vessel is very similar to that used in mechanical pattinsonising, having a pipe for the introduction of steam in place of the mechanical agitator. The steam is generally used at a pressure of about three atmospheres.

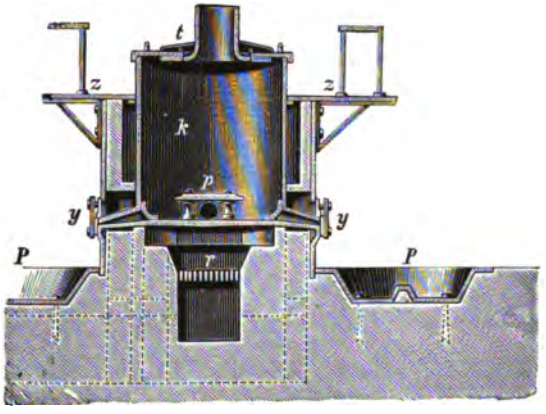


FIG. 314.

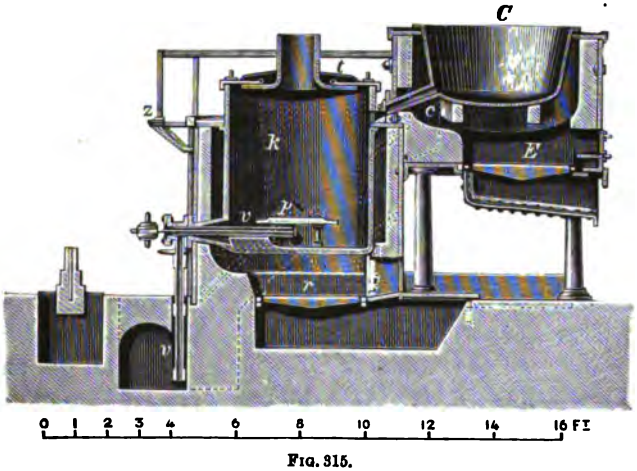


FIG. 315.

Figs 314 and 315 show the arrangement of the apparatus which is in use at St Louis les Marseille, near Marseilles. *C* is the melting pot heated by a fire on the grate *E*, and holding 9 to 10 tons of lead; *k* is the crystallising vessel of a capacity of 16 tons heated from the fireplace *r*. The melting pot has a spout *c* provided with a valve for running the molten lead into the crystallising vessel, and *v* is the

pipe by means of which steam is led into the latter, a cast-iron plate p being placed over the end of this pipe in order to better distribute the steam throughout the molten metal. There are two pipes, y, with valves for running off the mother liquor from the crystallising vessel, the mother liquor flowing into the cast-iron moulds P. From these the solidified lead is lifted by cranes, and if necessary put back again into the melting pot. The cover t of the crystallising vessel is composed of separate segments, which can be lifted independently

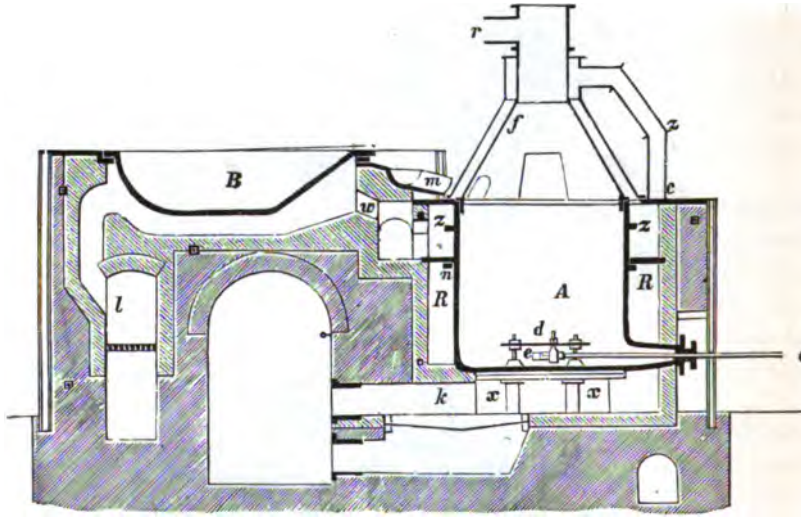


FIG. 316.

so that the contents can be easily observed and any incrustations loosened.

The arrangement of the plant in use at Przibram in Bohemia is shown in Figs 316, 317 and 318. A is the 20 ton crystallising vessel resting on the columns x, x, and the wall y, and surrounded by the flues R R. At a higher level are the two melting pots B, each capable of melting 7 tons of lead, and from these the molten lead is run into the crystallising vessel by slightly tilting the melting pots by means of a crane. From the grate k the hot products of combustion pass round the bottom and the sides of the vessel below the annular iron plate n, and then pass into the flue o. The portion of the vessel above the plate n is kept hot by means of the waste gases from the melting pots; after heating these pots they pass by the flue w to the crystallising vessel, circulate round the upper part of this, and then pass to the chimney through the flue p.

Steam is forced into the vessel through the pipe *e*, placed under the baffle-plate *d*, and the steam passes away through the hood *f*, of iron

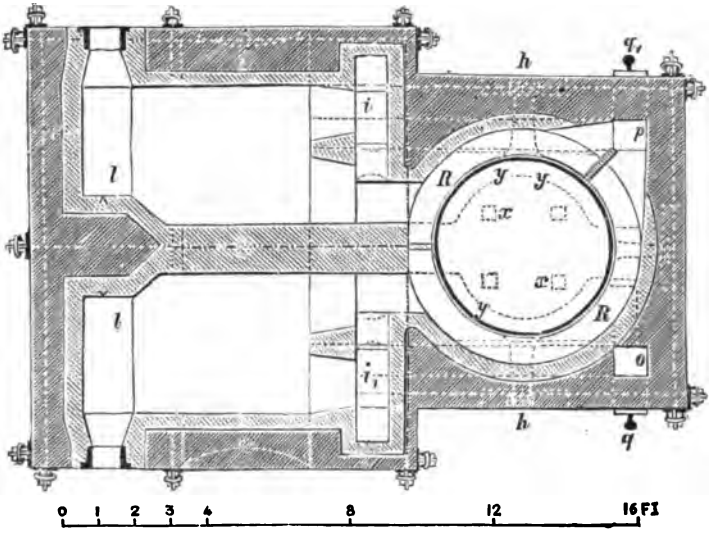


Fig. 317.

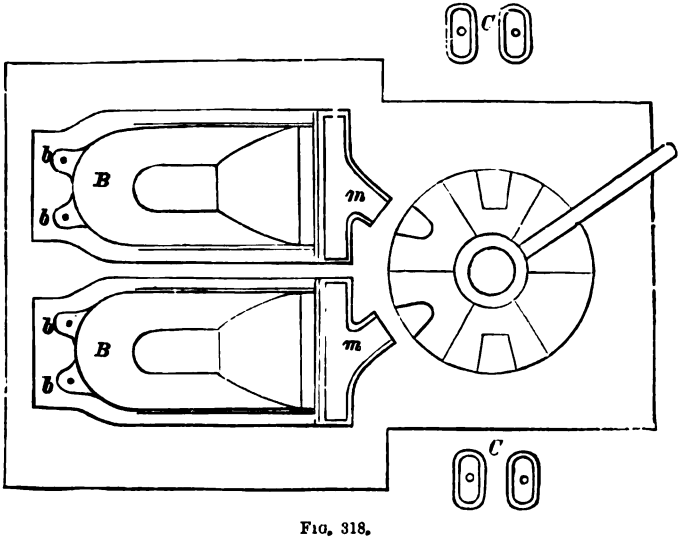


Fig. 318.

plate, provided with two working openings. This hood is surrounded by a second hood, also of iron plate, and by withdrawing a damper *g* hot waste gases from the flues can circulate in the space between the

two hoods. By this means the inner hood is heated, and any lead which may be splashed up against it by the bubbling of the steam can be caused to melt and flow back into the vessel. The waste gases pass along the pipe z' and away to the chimney flue. The mother liquor is drawn off through two spouts h provided with slide valves, and kept hot by the hot gases from fireplaces i and i'.

In working the Rozan process the system of thirds is generally adopted as in mechanical pattinsonising, and rich lead with 1·6 to 2 per cent. of silver, and poor lead with 0·001 to 0·003 per cent. of silver are obtained. The process is conducted as follows :—

The lead is first melted in the melting pots and any scums removed from the surface, and it is then allowed to flow into the crystallising vessel. Steam at three atmospheres pressure is forced through and thoroughly mixes the fluid lead with the crystals from the previous operation which were already in the vessel, quickly melting the latter. When completely fluid, crystallisation is induced by withdrawing the fire and allowing a small stream of water to flow over the surface of the lead, and when $\frac{2}{3}$ of the contents have assumed the crystalline state the scum of oxide is removed from the surface and the enriched lead is tapped off. A sufficient quantity of lead of the requisite silver content has in the meantime been melted in the pot so as to furnish another charge when added to the crystals remaining behind in the vessel, and the whole operation is repeated until the lead is sufficiently desilverised. In this process it is also necessary to have in reserve a variety of lead with various percentages of silver.

The process is in use in England at Newcastle-on-Tyne, in France at St. Louis les Marseille, Spain at Carthagena, Bohemia at Przibram, and at Eureka in Nevada State, U.S.A.

At St. Louis les Marseille, Spanish lead with about $\frac{3}{4}$ per cent. of impurity (less than $\frac{1}{2}$ per cent. of antimony) is enriched up to 1·8 per cent. of silver without any previous refining. Grecian leads with 5 per cent. of impurity (2·5 per cent. Sb, 1 per cent. As, 0·5 per cent. Cu), as well as lead from Pontgibaud with 3·2 per cent. antimony, 0·3 per cent. of copper, and much arsenic, are previously refined and enriched only up to 1·6 per cent. of silver. On an average some 13 operations are got through in 24 hours, lead with 0·123 per cent. of silver being worked in charges of 13 to 16 tons, yielding from each charge 6 to 7 tons of market lead containing 0·001 to 0·002 per cent. of silver. For each operation $2\frac{1}{3}$ cwts. of coke are used, about 202 lbs. for heating the pots, and 62 lbs. for raising steam. About 4 cwt. of oxide are formed from each ton of lead. This partly collects on the

surface of the molten metal, and is in part carried off by the current of steam and collected in condensation chambers ; it is chiefly litharge. The loss of lead amounts to 2·1 per cent., and that of silver to 1·5 per cent. as compared with the assay values.

The total cost of working 1 ton of lead is 25·85 francs. In the hand-worked Pattinson process the lead loss amounts to 3 per cent., the silver loss to 1·5 per cent., and the total cost amounts to 46·54 francs per ton.

At Przibram in Bohemia the work-lead is liquated before pattinsonising in order to get rid of copper, which is present to the extent of about 0·1 per cent. The crystallising vessel holds 20 tons, and each melting pot 7 tons of lead, and 6 to 7 operations are conducted every 24 hours. The melting of the metal takes 3 hours and the crystallising 1 hour, and the products are rich lead with 1·3 per cent. of silver, and poor lead with 0·001 per cent. of silver, the coal used amounting to 20 per cent. by weight of the lead treated. The desilverised lead still contains antimony, and it is therefore submitted to refining in a reverberatory furnace. The various products from 100 parts of lead are as follows :—

	Work-lead.	Silver in the work-lead.	Lead in the work-lead.
Rich lead	42·99	97·36	42·58
Poor lead	44·76	0·17	45·01
Drosses	3·02	0·61	3·03
Skimmings	9·94	1·45	8·04
Flue dust	0·46	0·07	0·35

The Rozan process is the cheapest method of conducting the operation of pattinsonising, and is therefore superseding the hand process and also the mechanical process. The cost for both fuel and labour is less than in either of the other processes, and the amount of scum and dross produced is also less.

Desilverising by means of Zinc

If argentiferous lead be melted, pieces of zinc forming altogether from 1½ to 2 per cent. of the weight of the lead thrown on its surface, the temperature of the bath raised to the melting point of the zinc, and the whole thoroughly stirred and then allowed to cool, a crust or scum forms upon the surface as the temperature is lowered. This scum is a solidified mixture of alloys of lead, zinc and silver, lighter than the molten lead and containing all the silver originally present

in the lead, and it can easily be separated from the rest of the metal forming the bath.

According to the researches of Rœssler and Edelmann, molten zinc dissolves lead and molten lead dissolves zinc, and the higher the temperature the greater the amount dissolved. If more of one metal is present than the other is able to dissolve at the particular temperature employed, the excess of metal separates out. These experimenters found that at temperatures between 350° and 650° lead dissolves from 0·6 to 3 per cent. of zinc, whilst zinc between the same temperatures takes up from 1·7 to 5·6 per cent. of lead. By melting together 100 parts by weight of lead with 10 parts of zinc they obtained :—

At 350° :	99·9	parts of lead	containing	0·6	of zinc and	9·4	parts of zinc	containing	0·1 of lead
,, 450° :	99·8	,,	,,	1	,,	9	,,	,,	0·2 ,,
,, 550° :	99·7	,,	,,	2	,,	8	,,	,,	0·3 ,,
,, 650° :	99·6	,,	,,	3	,,	7	,,	,,	0·4 ,,

And they also determined the melting points of zinc-silver alloys as follows :—

Composition of alloy.	Melting point.
90 of zinc and 10 of silver	450°C
80 ,, ,, 20 ,, ,,	550°C
70 ,, ,, 30 ,, ,,	650°C

Consequently, by melting zinc with argentiferous lead, 0·6 per cent. of zinc will always remain associated with the lead and will not separate out on cooling the bath of metal, whilst the remainder of the zinc, together with the silver and a certain proportion of lead, separates out on the surface. From this mixture of alloys, the zinc can be separated by distillation, oxidation, or treatment with fluxes, so that only silver and lead remain, whilst the zinc remaining in the lead bath can be eliminated by oxidation. It is thus possible by means of the zinc process to separate the lead into two portions, one rich and the other poor in silver.

The lead is rarely enriched so as to contain more than 12 per cent. of silver, whilst the amount in the poor lead is reduced to 0·0005 per cent. According, however, to the recently-devised process of Rœssler and Edelmann, it is possible to concentrate most of the silver in argentiferous lead in a silver-zinc alloy containing very little lead, and to obtain the silver from this alloy by means of electrolytic methods or by treatment with sulphuric acid.

The principle of the zinc process was first described by Karsten in 1842, but for a long time no satisfactory progress was made towards

its application on the large scale. The separation of the silver from the zinc-silver alloy could not be effected without great loss of metal, and the zinc remaining in the lead was only removed with great difficulty and expense. Parkes was the first to introduce the process on the large scale, and it was first worked in England in 1850–52, followed by its introduction in the later sixties into the Rhenish works in the Eifel, the difficulties mentioned having fortunately been overcome. From this time onward it has gained ground and promises to entirely supplant the Pattinson process. Its advantages over the latter process are a higher yield of lead and silver, and a more rapid separation of the two metals, so that market lead is more quickly obtained, whilst the much greater richness of the silver-lead alloy produced reduces considerably the expenditure in fuel and wages, and the market lead is purer than that ordinarily obtained in the Pattinson process.

In the zinc process the lead is desilverised until it contains only 0·0005 per cent. of the precious metal as against the 0·002 per cent. of the Pattinson process, and the rich lead can, without difficulty, be obtained with 12 per cent. of silver as against 2½ per cent. in the Pattinson process.

Of the various foreign metals present in the lead, the whole of the copper is found in the zinc alloy, and this constitutes a special advantage of the process, enabling a market lead practically free from copper to be produced.

All the gold passes into the zinc-silver alloy, but it is possible, by adding a smaller amount of zinc in the first instance, to obtain the whole of the gold of the argentiferous lead with only a portion of the silver, in the first scum or crust skimmed off from the surface of the bath, and this can then be worked up by itself to auriferous silver.

Nickel and cobalt also associate themselves with the zinc-silver alloy, whilst antimony remains with the lead, and if present in large amounts retains a certain quantity of silver. In quantities up to 0·7 per cent., it is, however, without injurious influence in this respect. Tin and arsenic remain with the lead. The presence of arsenic delays the process and hinders the complete separation of the zinc-silver alloy. Bismuth is found in the desilverised lead.

It will thus be seen that the presence of copper, nickel and cobalt, which associate themselves with the zinc, will occasion a large consumption of this metal, whilst antimony, arsenic and tin, remaining with the lead, necessitate a costly purification of the metal after desilverising. Consequently, lead containing a large percentage of these foreign metals, must be purified before being desilverised. Lead

containing only small quantities of copper and not more than 0·7 per cent. of antimony need not be previously refined, as the copper is removed by the zinc in desilverising, and the antimony is eliminated in the softening process which the desilverised metal must undergo for the removal of the small amount of zinc taken up in the process.

Bismuth, which remains with the lead, cannot be eliminated by liquation or refining, as it neither forms a difficultly fusible alloy with lead like copper does, nor can it be separated from lead by oxidation. It can only be separated by using the Pattinson process, when the bismuth collects in the rich lead, and when the silver has been eliminated to a certain extent, the poor lead is found to be practically free from bismuth. At Freiberg, the lead contains, to begin with, 0·4 to 0·8 per cent. of silver, and it is found that when the silver content has been reduced to 0·1 per cent. by pattinsonising, the lead is practically free from bismuth. It is for this reason that the two processes of desilverising are worked in conjunction at Freiberg, the lead being partially desilverised by the Pattinson process, and the operation completed by the zinc process.

The process of desilverising by means of zinc comprises two operations:—

1. The separation of the argentiferous lead into poor lead and an alloy of lead, zinc and silver.
2. The production of a rich silver-lead from the zinc alloy.

I. The Production of the Silver-Lead-Zinc Alloy from Argentiferous Lead

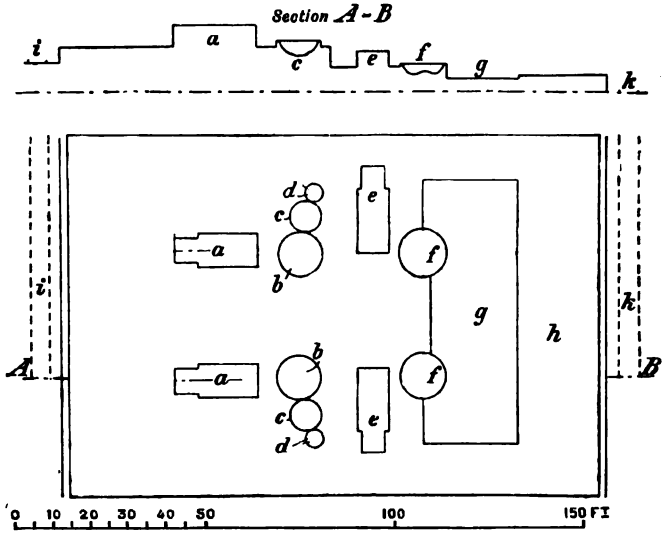
Before applying this process to impure leads, a refining operation is necessary. Under all circumstances the desilverised lead must be refined in order to get rid of the small amount of zinc and of antimony if the latter be present. The alloy produced in desilverising contains a considerable amount of lead, part of which is got rid of by liquation before the alloy is treated further.

All these different operations: the preliminary refining, the production of the alloy, the liquation of the alloy, and the refining (dezincising) of the desilverised lead are carried on in such a way in a series of apparatus that the lead remains from beginning to end in the fluid state, and all cost of transport is saved, except indeed in those cases where it is necessary to pump or syphon the lead into the first apparatus of the system.

The refining of the work-lead, or if much copper is present, the liquation of the work-lead, is carried out as described in detail on

page 443 in reverberatory furnaces. The desilverising proper is effected in cast-iron or, more rarely, cast-steel pots. The liquation of the lead from the mixture of alloys is performed in pots of cast-iron, whilst the refining of the desilverised metal is effected in reverberatory furnaces, or in cast-iron or cast-steel pots.

In order to save expense in transferring the lead from one vessel to another for these various operations, it is advisable to arrange the apparatus in terrace form, the furnace for the preliminary refining being on the highest level. On the next terrace come the desilver-



FIGS. 319 AND 320.

ising and liquating pots, and below on the next lower level the apparatus for refining the desilverised metal. Below this again comes the vessel for receiving the refined lead, and at the lowest level the moulds in which the lead is cast into pigs.

A plant arranged on these principles, typical of the practice in North America, where impure lead is generally treated by the zinc process, is shown in Figs. 319 and 320; *a*, *a* are the refining furnaces for the work-lead, and on the next level are placed the desilverising pots *b*, *b*, with the liquation pots *c*, *c*, and the pots *d*, *d*, for receiving the liquated alloy; *e*, *e* are the furnaces for refining the desilverised lead, and *f*, *f*, the vessels for receiving it. In the lead pit *g* the casting takes place, and *h* is the weighing platform. The lead comes to the plant along a line of rails at the level *i*, and the desilverised lead leaves it at *k*.

Instead of the reverberatory furnace, the refining of the lead is also carried out in pots, and in such a case they would take the place of the furnaces *a*, *a*, on the uppermost level, but in the States, refining in furnaces is the more general method, pots lasting only for a short time.

When all the apparatus is on one level, which is usually the case on the Continent, where the preliminary refining is not generally necessary, then the final refining is done in the same vessel in which the lead has been desilverised, and the liquation of the lead in pots lying beside the latter. The market lead in this case must be pumped out of the vessel by means of a Rösing lead pump unless a lower level is available so that it can be syphoned off.

By arranging the apparatus in terraces, the expenditure in wages is diminished and the capacity of the plant is greater than when all the parts of it are placed on the same level. The former arrangement in particular is preferable where a preliminary refining of the lead is necessary.

As already mentioned, the desilverising is effected in cast-iron or cast-steel pots similar to those employed in the Pattinson process, and in many places on the Continent the plant employed in the process of hand pattinsonising has simply been used for the zinc method. The capacity of the pots varies from 12½ up to 55 tons of lead, those in use on the Continent seldom exceeding 25 tons, whilst in the United States they do not usually carry less than 30 tons. Elliptical pots are also in use, such as those employed at the works of the Omaha and Grant Smelting and Refining Company at Omaha in Nebraska, holding 48 tons; and of other large pots of circular section may be mentioned the recent vessels at the Balbach Works, near Newark, New Jersey, holding 50 tons; at Cheltenham, St. Louis, 38 tons; the National Works, Chicago, 35 tons; and the Pittsburg Works, with 50 ton vessels. Amongst vessels of small capacity are those at Lautenthal, Altenau, and Oker, holding 12½ tons; at Friedrichshütte, Upper Silesia, 14 tons; and the Rhenish desilverising plants holding 20 ton charges.

Vessels of large capacity have the advantage over small ones in using less fuel and particularly in economising labour. A capacity of 30 tons may be taken as a fair average when the plant is arranged in terrace form, but if the desilverised lead is to be refined in the pot by means of steam, the charge for such a pot should not exceed 25 tons. The pots are generally from 3 feet to 3 feet 3 inches in depth, the diameter depending on the capacity. For instance, a pot of 30 tons capacity, 3 feet 3 inches deep, would measure internally 8 feet 10 inches at the top. An elliptical vessel of 55 tons capacity measures

39 inches in depth and is 12 feet long and 7 feet wide internally. The thickness of the metal is often greater at the bottom than at the sides, for instance, 2 to 2½ inches at the bottom, as against 1½ to 2 inches at the upper part, though at the present time vessels are being made of an equal thickness throughout and seldom more than 1½ inches thick. Pots of this thickness last 1—1½ years, provided that they are only employed in desilverising, and are not raised to higher tempera-

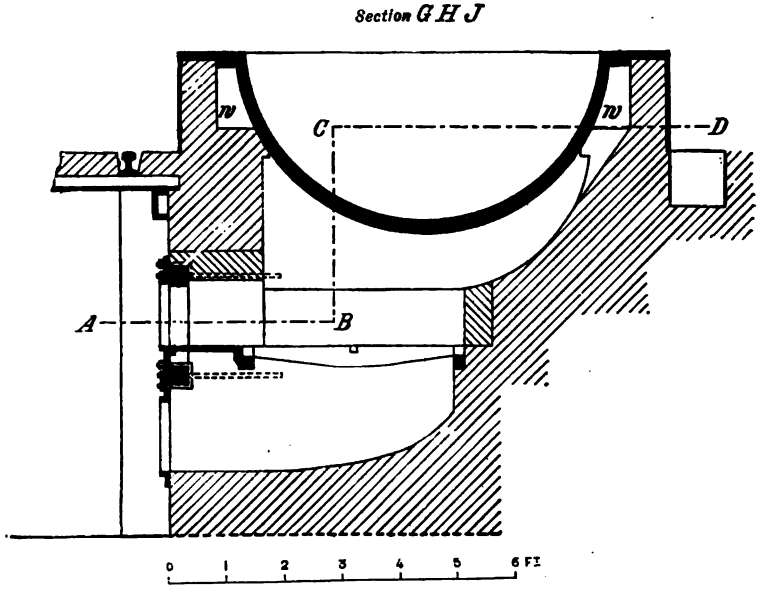


Fig. 321.

tures. If they are also used for refining, their life is much shortened, extending only to some 30 to 60 charges with impure lead.

Cast-steel pots are only used when refining and desilverising are conducted in the same pot as, for instance, at Friedrichshütte, in Upper Silesia. If made of crucible steel these stand from 250 to 270 charges, and if of open-hearth steel, from 120 to 150 charges. This extraordinary durability has not been reached at other places where they have been tried (Hoboken, Antwerp) and must be attributed to the quality of the work-lead at Friedrichshütte, which only contains very small amounts of antimony.

The method of setting the pots has already been explained in considering the refining of lead and the Pattinson process (p. 437). The exact arrangement of a pot with its fire grate is shown in Figs. 321 to 324, representing one in use at Lautenthal in the Upper

Harz. In a pot of this kind arranged with the rest of the plant on the same level, only 12½ tons are desilverised at a time. The terrace or platform system of arrangement is shown in Figs. 325 to 328, which represent the plant in use at Freiberg.

The two desilverising pots *a*, *a*, are placed on the same level as

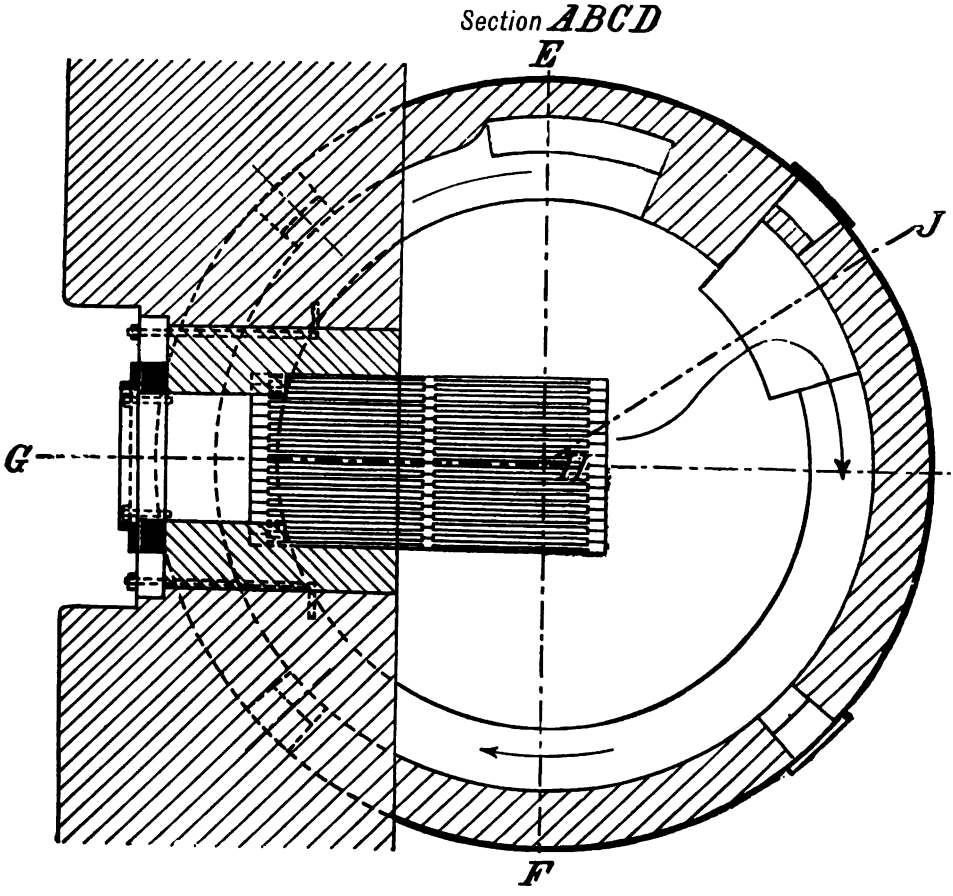


FIG. 322.

the liquation pots *b*, *b*, lying between them. The former are 5 feet 2 inches in diameter, 3 feet 3 inches deep, and hold 20 tons of work lead. The hemispherical liquation pots *b*, *b*, are of 21½ inches radius. Below the desilverising pots stands the refining furnace *c* for freeing the desilverised lead from zinc, the lead being discharged from the

pots into it by means of a syphon. The furnace is 9 feet 10 inches long, 6 feet 7 inches broad and 17½ inches deep, with a hearth constructed of fireclay lying 6 feet below the rim of the desilverising

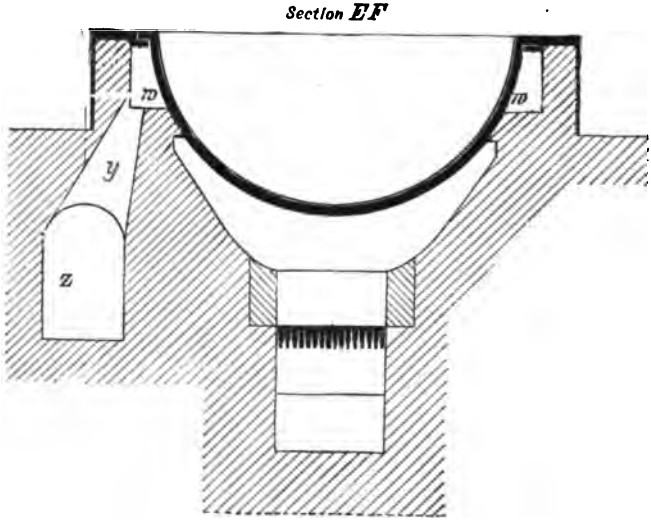


FIG. 323.

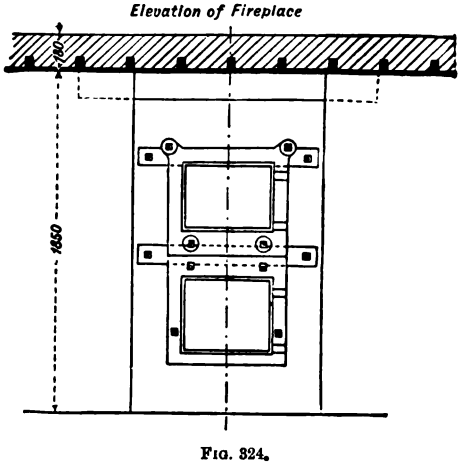
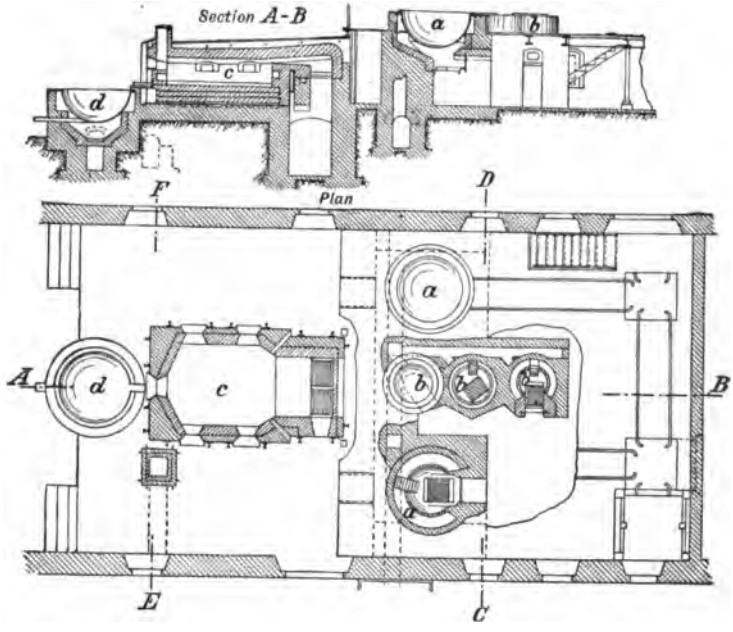


FIG. 324.

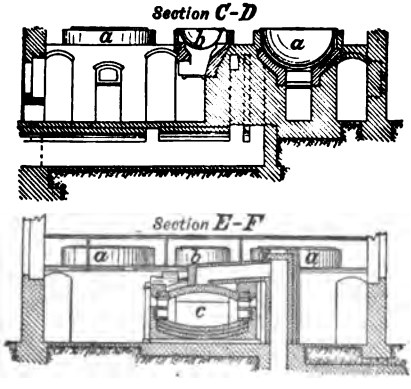
pot. Below the refining furnace is a cast iron tapping pot *d*, 6 feet 3 inches in diameter and 3 feet 3 inches deep, into which the desilverised lead is allowed to flow through a pipe furnished with a conical valve.

The Desilverising Process.

If the lead requires refining before desilverising, it is allowed to flow from the refining furnace standing above the desilverising vessel



Figs. 325—326.



Figs. 327—328.

into the latter. The vessel must be previously warmed and coated inside with milk of lime in order that the scums can be easily separated from its sides. The lead is either tapped into the pot or

syphoned over into it. In the former case it flows through a cast-iron spout, and in the latter, into a cast-iron pipe placed vertically in the pot, the formation of crusts being thus lessened. These crusts which form on the surface and have to be ladled off, constitute about 1 per cent. of the weight of the lead.

If it is not necessary to refine the work-lead it is put directly into the desilverising pot and there melted. After melting, the scums are removed and then the treatment with zinc commences, as is also the case with the refined lead. If the lead is poor in silver the zinc is added in two portions, if rich in silver usually in three, and when much gold is present, four or even five separate additions of zinc are made.

The total quantity of zinc to be used in desilverising depends upon the amount of silver in the work-lead, the richer the work-lead the more zinc being required. Poor leads use proportionately more zinc, because, in any case, the lead takes up 0·6 per cent. of zinc which plays no part in the desilverising.

According to Illing[1] the amount of zinc in percentages of the work-lead, required for lead with various percentages of silver is as follows:—

Silver in work-lead per cent.	Zinc required per cent.
0·025	1·25
0·05	1·33
0·1	1·5
0·15	1·66
0·4 } 0·3 }	2·0

According to Junge[2] the zinc consumed (as in the previous case, not counting the zinc recovered again by distillation) is as follows:—

Silver in work-lead per cent.	Zinc required per cent.
0·0963	1·34
0·3825	1.84
0·508	1·96
0·84	2·45

The amount of zinc does not depend entirely upon the silver percentage of the work-lead but will also be influenced by the amount

[1] *Preuss Zeitschr.*, 1868.
[2] *Freiberger Jahrbuch*, 1889, p. 6.

of copper and of gold present. The total quantity of zinc, as also the number and weight of the charges, required for different varieties of work-lead can easily be ascertained by experiment, and a table can then be drawn up showing the amount of zinc necessary when various percentages of copper, silver and gold are present.

Only pure zinc must be used, and the use of impure metal and scrap zinc has not proved economical in spite of their lower price.

If copper and gold are present in the lead, these metals are taken up by the zinc before the silver and, indeed, before the lead itself is saturated with zinc. According to Hofmann[1] 30 tons of lead requiring 396 lbs. of zinc (0·6 per cent.) for saturation, yielded 0·30 ounces of gold per ton (0·0009 per cent.) in the scum formed after adding 330 lbs. of zinc.

In practice a double advantage is gained, owing to these facts. In the first case by adding a proportionately small amount of zinc in the first instance, the copper and gold can be separated, and again, after separating the copper in this way, the later zinc additions which are not saturated with silver can be used over again for desilverising as they are quite free from copper and by their use copper is not introduced again into the bath.

The zinc is usually added in flat ingots thrown on to the surface of the molten lead, the temperature of which is then raised to the melting point of zinc. In order to avoid oxidation of the zinc it may be placed at the bottom of the metallic bath in a perforated box and there melted, or it may be melted separately and poured into the molten lead.

After the zinc is melted, it is intimately mixed with the molten lead either by stirring with a perforated paddle or by a mechanical agitator, or else by means of steam, the usual way being by means of the paddle. After stirring for half an hour the bath of metal is allowed to cool slowly, and the alloy of lead, silver and zinc with copper and gold, if these metals are present, gradually collects on the surface. This is generally removed as fast as it forms by means of a perforated ladle, and this is continued until crystals of lead begin to form on the surface and the lead begins to solidify on the sides of the pot.

The temperature of the bath is now increased and a second portion of zinc is added, and the operation repeated precisely as after the first addition, and at many works a third and fourth addition of zinc is made. If the lead is auriferous, the gold will be found in the first scum removed.

[1] *The Metallurgy of Lead*, p. 328.

When the assay shows that the silver content of the lead has been reduced to 0·0005 to 0·0006 per cent. the process is stopped, or if more silver than this is present, zinc is added until it is reduced to this amount.

In the Upper Harz, the charge consists of 12½ tons of work-lead containing 0·14 to 0·15 per cent. of silver, and this is desilverised without any previous refining down to 0·0005 per cent. of silver. At Lautenthal, where this process was used, though it has now been replaced by the aluminium-zinc process, the first addition of zinc weighed 48 lbs. This first portion of zinc takes out the gold and copper, the silver in the alloy formed not amounting to more than 0·18 or 0·19 per cent., and this first alloy was worked up separately on account of the gold in it. The second zinc addition amounted to 110 lbs., and at the same time the scum previously obtained after the third zinc addition was also added as it was not saturated with silver. This second zinc addition abstracted the bulk of the silver from the lead, so that, after removing the scum, the silver was brought down to about 0·02 per cent., and in order to take out this last portion a third addition of 180 lbs. of zinc was made. In this way an alloy which was still capable of taking up more silver was obtained, and this was added again with the second lot of zinc.

The alloys ladled from the pot and known as zinc scums were put into a pot close beside the large one and as soon as this was filled the alloy was liquated. The refining of the desilverised lead was then proceeded with in the manner previously described (page 440). The entire process, including the melting of the lead, lasted 21½ hours, the time taken in the various operations being as follows:—

Melting the work-lead	6 hours
Melting and stirring in the first zinc	½ hour.
Cooling the bath and removing the cupriferous scum	2½ hours.
Reheating and melting the second zinc	3 „
Stirring in the zinc	½ hour.
Cooling the bath and removing the first zinc scum	3 hours.
Reheating the bath and melting the third zinc	2 „
Stirring in the zinc	½ hour.
Cooling the bath and removing the second zinc scum	3½ hours.

The consumption of fuel for desilverising, including that used in the subsequent refining which follows on immediately in the same pot, was 9·76 tons of coal and 140 faggots of brush-wood for every 100 tons of work-lead.

At Friedrichshütte, Upper Silesia, the pots are also placed side by

side and the refining and desilverising operations are both conducted in the same vessel. The pots are of cast steel and each hold 13·5 tons of work-lead. In the year 1893, according to a communication from Inspector Laske, lead from the Tarnowitz reverberatory furnace process with 0·04 to 0·05 per cent. of silver, lead from blast furnace smelting with 0·024 to 0·028 per cent., and rich lead with 1·2 per cent. of silver, left after distilling the zinc scums, were desilverised by this process. Two additions of zinc were required for the reverberatory furnace lead, three for the blast furnace lead, and five for the rich lead, and the lead was desilverised until it only contained 0·0003 per cent of silver.

The consumption of zinc reckoned on the refined work-lead amounted to 1 per cent. for the reverberatory furnace lead, 1·3 per cent. for the blast furnace lead, and 2·5 per cent. for the rich lead. The desilverising lasted from 28 hours for the work-lead, to 48 hours for the rich lead, and the consumption of coal varied from 7·4 per cent. of the weight of the lead used, or 8 per cent. of the weight of market lead obtained, up to 10 per cent. of the weight of the rich lead including the coal used in refining.

At the Mulden Works in Freiberg [1] lead containing 0·1 per cent. of silver is submitted to this process. The charge employed is 20 tons of lead, and three additions of zinc are made at intervals of five hours, the first addition consisting of 220 lbs., the second of 165, and the third of 89 lbs., the total amount of zinc used being 474 lbs., equal to 1·485 per cent. of the charge of lead. The first zinc addition reduces the percentage of silver from 0·1 down to 0·025 per cent., and takes out also the greater part of the gold present. The second addition reduces the silver to 0·002 per cent., and the third to 0·0007 per cent., the addition of zinc being discontinued when the proportion of silver is reduced to 0·001 per cent. The scums are ladled into the liquation pot and freed from a part of the lead they contain by liquation. The desilverising operation lasts 20 hours, 5 hours for melting and skimming the work-lead, and five hours for each addition of zinc.

In the United States lead containing 0·75 to 1 per cent. of silver is treated by this process. It is refined before desilverising, and is run in the molten state into the desilverising pot so that the added zinc quickly dissolves and the desilverising proceeds rapidly. If the lead is auriferous, 3 to 5 additions of zinc are made at five-hourly intervals with a 30 ton charge. Working quickly and carefully it is possible to work off 30 tons with 4 zinc additions in 18 hours. If the gold and silver scums are taken off together, 45 tons can be desilverised in the

[1] Plattner, *Jahrbuch für das Berg- und Hüttenwesen im Konigreich Sachsen*, 1886.

same time. The coal consumption is about 3 per cent. of the weight of the unrefined lead.

At Omaha 48-ton charges are desilvered in large elliptical pots, three additions of zinc being made, the last scum being used over again for desilverising. The consumption of zinc is 1·5 per cent. of the weight of the lead, and the zinc scum contains 3000 ounces of silver per ton.

At the National Works, at Chicago, 32 to 35-ton charges are desilverised in round pots heated by paraffin oils, a charge being worked off in 12 hours, and at Pittsburgh, where natural gas is employed for heating, 50-ton charges are worked in the same time.

At the St. Louis' Smelting and Refining Company's Works, at Cheltenham, St. Louis, the average charge is 36 tons of work-lead. Two additions of zinc are used, and the operation takes 15 hours, an interval of 6 to 7 hours intervening between the two additions of zinc. The consumption of the latter metal amounts to 1·5 per cent. of the weight of the lead which contains 250 ounces of silver per ton (0·777 per cent.), and 1·25 tons of coal are used for each pot in 24 hours.

At Port Pirie, in South Australia, part of the output of lead from the Broken Hill Proprietary Company is desilverised. It contains from 250 to 350 ounces of silver per ton (0·777 to 1·088 per cent.), and is refined before desilverising, being then run into the desilverising pot of 20 tons capacity, in charges of 19 tons. Three zinc additions are used, and the coal consumption amounts to 3·4 per cent. of the lead desilverised, the operation lasting 24 hours.

Liquation of the Zinc Scums

The zinc scums taken off from the bath still retain a very considerable proportion of lead, and this excess of lead is as far as possible removed before the next operation. This removal is rendered possible owing to the fact that the alloy has a higher melting-point than lead itself, so that if it be heated to the melting-point of lead, a good deal of this metal drains away, leaving the solid alloy behind, and the higher the temperature the more lead is removed. When the temperature reaches a certain point, oxidation of the zinc and lead takes place, and a mixture of oxides of zinc with various oxides of lead and the triple alloy, floats on the surface of the bath. If the temperature be raised still further, argentiferous lead is obtained, and a mixture of oxides of lead and zinc, and in this case that part of the silver that was previously combined with the zinc oxide goes back again into the lead. If the zinc oxide could be thus obtained in a pure state, the separation of the zinc from the alloy would be a simple

matter, but it forms a tough pasty mass with the oxide of lead and retains mechanically a good deal of the alloy, rendering a complete separation impossible. If the oxide of zinc be present in large pro-

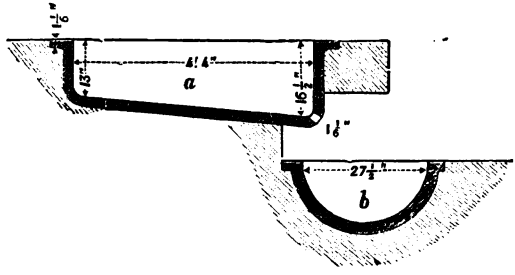


FIG. 329.

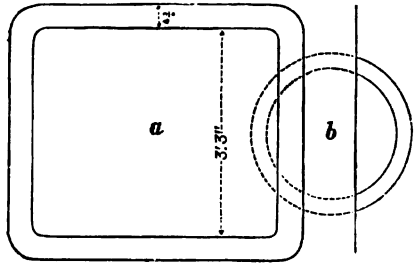


FIG. 330.

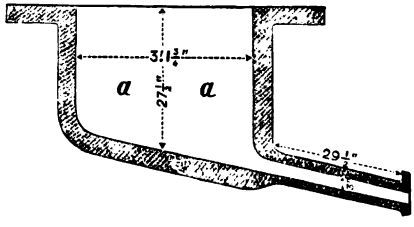


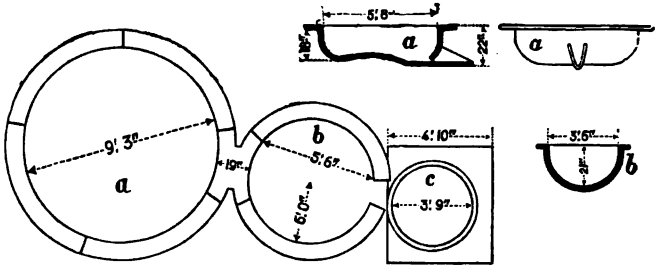
FIG. 331.

portion, the mixture no longer melts, owing to the infusibility of zinc oxide.

Owing to these circumstances the amount of lead that can be liquated out from the alloy mixture is dependent on the manner in which the alloy is to be treated subsequently. If the zinc is to be separated by passing steam through the molten alloy, the liquation must not be carried far, as the presence of zinc oxide interferes with its fusibility, whereas if the distillation method is adopted

the liquation can be carried much further, as any oxides formed would be reduced when heated with charcoal in the distilling vessel.

The liquated alloy is known as *rich scum*, and the process of liquation is carried out either in pots or reverberatory furnaces. Pots are usually used in the smaller works and in those cases where the zinc is separated from the rich scum by distillation. They are made of cast iron and most advantageously placed beside the desilverising pots. They must be provided with an exit pipe at the bottom, if the rich scum is to be subsequently treated by the distillation process, vessels without exit pipes being only used where the rich scums are melted and treated by steam to free them from zinc, in which case scums rich in lead are left. In this latter method a *dry* zinc scum or one poor in lead is not produced, because on raising the temperature of the rich scum separated out on the surface of the bath, a portion of the



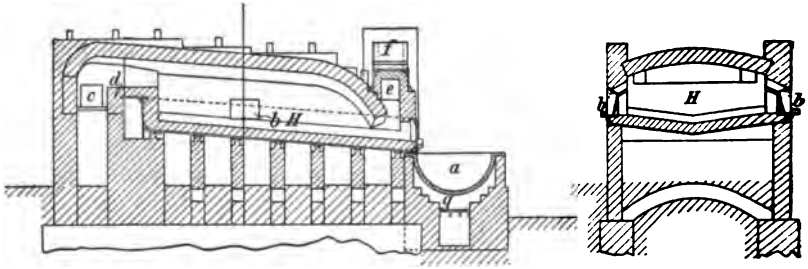
FIGS. 332—335.

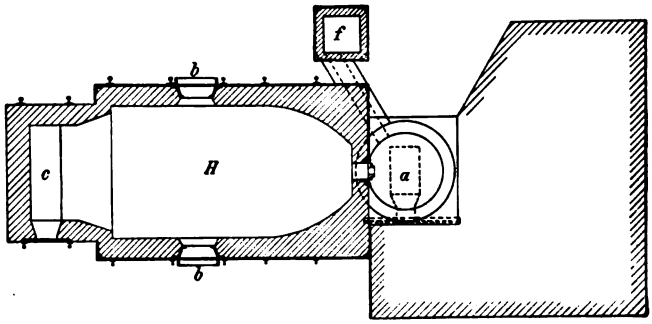
liquated lead is again dissolved, separating out on the cooling of the bath as a scum very rich in lead. If pots without exit pipes are used for the liquation of zinc scums which are to be distilled, the rich scum obtained by the first liquation must be submitted to a second treatment.

Pots without exit pipes are generally the desilverising pots themselves, if the rich scum is to be treated with steam, otherwise they are much smaller vessels. Pots with exit pipes are of various shapes, Figs. 329, 330 and 331 showing some which are in use on the Continent, the liquated lead flowing from them into pots at a lower level. The pots in use in the United States are shown in Figs. 332–335,[1] the liquation pots being constructed with convex bottoms, so as to allow of the spout being made as short as possible. The three connected vessels show how the plant is arranged, *a* being the desilverising pot, *b* the liquation pot, and *c* a smaller vessel for receiving the liquated alloy, each vessel having a separate fireplace.

[1] Hofmann, *The Metallurgy of Lead.*

The liquation apparatus in use at Freiberg is shown in the Figs. 325–328. The reverbatory furnace produces a dry rich scum, in a shorter time, and the formation of oxide is not greater than when





FIGS. 336—338.

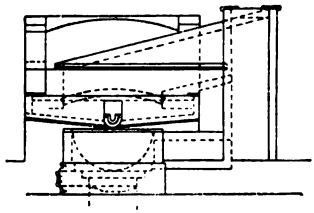


FIG. 339.

the operation is conducted in a pot, owing to the reducing atmosphere that is maintained.

The hearth is constructed either of cast-iron or fire clay, and in front of the sloping hearth is placed a heated pot to receive the liquated lead. The cast-iron hearth rests upon a layer of powdered fire-resisting material stamped into a wrought iron pan and is 10 feet long, 5 feet broad, and 4 inches high, having a slope of 3 inches

towards the exit spout, and the furnace has two working doors on each of the long sides.

The hearth of the furnace in use at Omaha consists of a wrought iron pan lined with a close bed of firebrick 9 inches thick, 12 tons of zinc scums being liquated in this furnace in 24 hours.

The liquation furnace in use at the Broken Hill Proprietary Company's works at Port Pirie, South Australia, is represented in Figs. 336 to 339; *c* is the fireplace, *b*, *b* are the working openings, *a* is the pot, placed before the furnace in order to receive the liquated lead, and heated by the fireplace *g*. The waste gases pass through the flue *e* into the chimney *f*.

The charge for this furnace is 1¾ to 2 tons of zinc scum, and this amount is liquated in four hours, using 308 lbs. of coal and requiring the attendance of one workman.

At Freiberg, the liquation, which is conducted in small pots, is repeated a second time, the zinc scum produced in the first pot being ladled over into the second and again liquated there. The lead obtained in this process containing 0·03 per cent. of silver and 1·3 per cent. of zinc, is again desilverised.

The two products of the liquation process are rich scum and liquated lead. The rich scum contains 1 to 10 per cent. of silver, and if it is to be melted and dezincised by steam it must be rich in lead, and contain therefore less silver than scums which are to be deprived of their zinc by distillation. Scums of this character obtained at the Altenau and Lautenthal works had, according to Rösing, the following composition:—

	Rich scum from Altenau work-lead.	Rich scum from Lautenthal work-lead.
Lead	75·675	77·82
Lead oxide	4·75	4·00
Zinc	11·78	12·11
Zinc oxide	0·60	0·44
Copper	1·12	0·82
Silver	1·855	2·42
Bismuth oxide	1·72	0·37
Antimony „	0·63	0·98
Arsenious „	traces	——
Ferric „	1·87	1·04
Cadmium	traces	traces
Nickel	traces	traces

At Lautenthal 100 parts of work-lead yielded 6 parts of rich scum.

The Freiberg rich scum which is submitted to distillation forms on an average 2·25 per cent. by weight of the work-lead and contains 0·0153 per cent. of gold, 4·051 per cent. silver, 53·2 per cent. lead, 2·68 per cent. copper, and 39·7 per cent. of zinc. The scum formed after the first zinc addition forms 1·73 per cent. of the work-lead after liquation, and contains 0·0174 per cent. of gold and 4·67 per cent. of silver.

The scum formed on the second zinc addition constitutes after liquation 0·31 per cent. by weight of the work-lead and contains 0·0016 per cent. of gold and 2·53 per cent. of silver, and that obtained after the third zinc addition forms 0·21 per cent. of the work-lead, and contains a trace of gold and 1·3 per cent. of silver.

The scums obtained in the United States works (Newark, Pittsburgh, Cheltenham, Chicago, Aurora, Kansas City, Omaha, Pueblo) contain from 4 to 10 per cent. of silver, and are generally submitted to distillation.

The lead liquated from the scum retains a considerable amount of silver and is put back again into the lead to be desilverised, the silver content of the liquated lead at Freiberg being 0·032 per cent.

In the United States the liquated lead from work-lead with $\frac{3}{4}$ per cent. of silver contains 0·3 to 0·6 per cent. of silver, if from the auriferous scums, and 0·093 to 0·1244 per cent. of silver if from the first zinc scum.

Treatment of the Desilverised Lead

The desilverised lead is either refined directly in the desilverising pot or it is run into a special refining pot or refined in a reverberatory furnace. If antimony is present it must be got rid of before the zinc can be removed.

The various methods of refining have been previously dealt with (page 430).

The consumption of fuel in refining the work-lead, desilverising the same, liquating the zinc scums and refining the desilverised lead in reverberatory furnaces, averages in America 330 pounds of coal for each ton of work-lead, that is, 14 to 15 per cent. of the weight of the work-lead.

At the Lautenthal works the consumption of fuel for desilverising the lead, liquating the scums and refining the desilverised lead amounts to 9·76 per cent. of the weight of the work-lead, the refining being in this case conducted in the desilverising pots which last about 30 charges.

At Port Pirie the pots in which the desilverising is carried on last 150 charges, but the refining pots only 50 charges.

At Cheltenham, St. Louis, 300 charges of 36 tons each are worked off in the one pot, and a larger pot of 48 tons lasted half a year at Omaha, having had in it 300 charges.

The Production of Rich Lead from the Zinc Alloy

This is effected by the separation of the zinc from the alloy, for which purpose the following methods may be used:—

1. Distillation of the zinc from the rich scum.
2. Smelting the rich scums with ferruginous slags in blast furnaces.
3. Separation of the zinc by cupellation.
4. Melting the scum with alkaline chlorides.
5. Oxidising the zinc by steam and dissolving out the zinc oxide formed from the resulting mixture of oxides of lead and zinc, and argentiferous lead.

Endeavours have also been made to separate the zinc electrolytically, but so far without success.

The only methods in which the zinc is recovered are the first and fifth processes, the zinc in the first case being obtained in the metallic state and in the latter process either as basic carbonate, oxide or sulphate. In all the other processes the zinc is lost.

In the distillation process, the zinc is recovered in the metallic state, and as this may be used again for desilverising, this process is to be preferred to the others on account of the high price of zinc. This is the case in spite of various imperfections in the process, and a lower yield of silver than in some of the other methods. Only in the case of auriferous copper scums which contain less zinc in proportion, and that chiefly in an oxidised condition (blue powder), is the smelting process or the steam dezincising to be preferred.

The method by which the zinc is obtained as basic carbonate, oxide or sulphate, even though it gives a higher yield of silver than the distillation process, can only be used when a market can be found for these products at a high price.

The smelting of the rich scums with ferruginous slags in blast furnaces is the least costly method of separating the zinc, but it is attended with considerable loss of silver and with the loss of the whole of the zinc, and can only be used when the price of zinc is very low.

The separation of the zinc in the cupellation furnace entails the loss of all the zinc and of considerable quantities of silver, and is practically not in use.

Melting with alkaline chlorides also occasions considerable silver loss, and the zinc is converted into a worthless slag, so that this method cannot be recommended.

1. The Distillation of the Zinc Scums

By means of this process the zinc can be quickly recovered from the scum mostly in the metallic state, though there is a certain loss of silver and zinc by volatilisation owing to leakages in the retorts, and the retention of silver and zinc in the retort residues. In other respects the process is very simple. The scum is heated above the boiling point of zinc in a retort provided with a receiver, the zinc volatilises, condenses partly as metal and partly as oxide, or wholly as oxide, and the argentiferous lead remains behind in the receiver.

The material of which the retort is made must be such that it is neither attacked by the lead in the scum nor by the ashes of the fuel, and consequently plumbago crucibles are chiefly used, or clay crucibles with a graphite or charcoal lining. The vessels are either tubes, pear-shaped retorts, or crucibles, and the receivers either old retorts or conical or pear-shaped clay tubes, or else vessels of cast-iron.

The furnaces used for heating the retorts may be made movable, so that they can be tilted, or they may be fixed, and they are heated with coal, coke or gas. The best and cheapest form are fixed tubular furnaces heated by gas, and these are usually employed except under certain local conditions.

Movable furnaces or tilting furnaces are at present heated only with coke. Faber du Faur has introduced such a furnace heated by gas or coal, but it has not come into actual use.

Coke-fired tilting furnaces called Faber du Faur furnaces after their inventor are in general use in the United States, and were first introduced at the Balbach works at Newark, New Jersey. Such a furnace is also in use at the works at Mechernich.

These furnaces are almost cubical in shape, supported on trunnions, and movable in much the same manner as a Bessemer converter. Each furnace holds only one retort. The arrangement of such a furnace is shown in Figs. 340 to 344. The sides of the furnace are of iron plate, lined with fire-clay, the top being formed by an arch *d* having an opening *o* for the introduction of the coke. The retort *r* is pear-shaped and rests on a small fire-clay support *f*, which in its turn is supported on a bed of fire-brick. The latter is either supported on an arch as shown in the drawing, or else rests on an iron plate ; *h* is the flue, and *v* the grate of wrought iron bars placed on edge. The furnace is tilted by the worm *s*, gearing into the toothed wheel *z*. Such a

furnace measures about 5 feet on each side, and holds 264 lbs. of rich scum, but at present larger furnaces are being used, holding 8 to

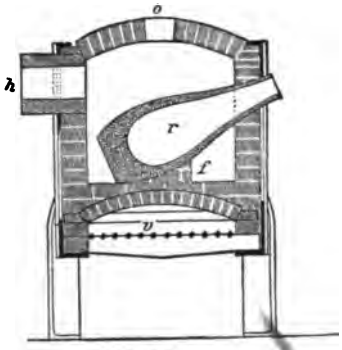


FIG. 340.

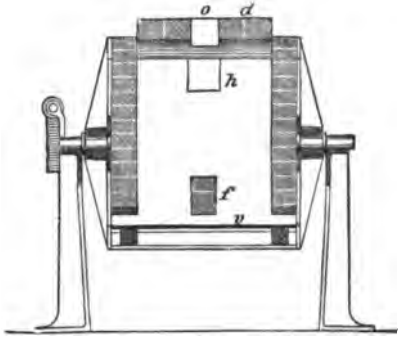


FIG. 341.

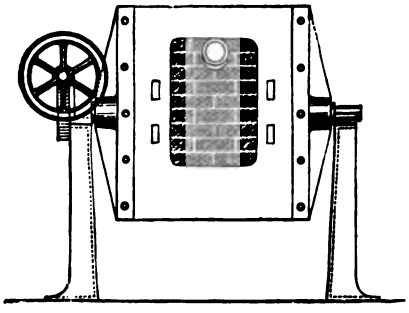


FIG. 342.

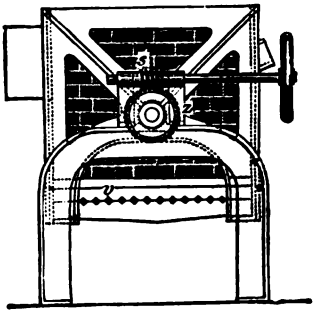


FIG. 343.

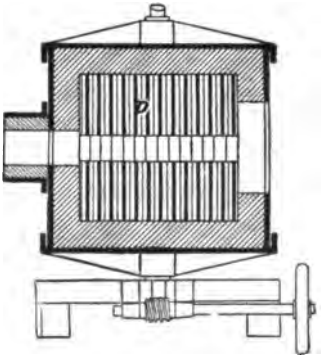


FIG. 344.

10 cwts. of rich scum, and the lining, which in the earlier furnaces was $4\frac{1}{2}$ inches thick, is now made only half that thickness, and in some cases the walls are water-jacketed.

The retorts were formerly made of a mixture of raw and burnt clay, with 25 per cent. of graphite, but at present they are made of graphite, with just sufficient clay to make it coherent, the proportion of graphite according to Hofmann [1] being 50 per cent. A retort to hold 8 to 9 cwt. of scum is 3 feet high, 8 inches in diameter at the neck, 18 inches at the belly, and 13 inches at the bottom. The walls are $1\frac{1}{8}$ inches thick at the neck increasing to 2 inches at the bottom. The separate furnaces are either arranged side by side along one side of a main flue, or else on either side of the flue, or arranged in a group of six or eight furnaces around a central chimney.

The working of the retorts consists in first charging them with the rich scum, mixed with 1 to 3 per cent. of charcoal, and then quickly raising the temperature to a white heat, and maintaining it at that point. After filling the retorts, the condenser, made out of an old retort is attached, and the joint made tight with clay. The higher the temperature the more quickly the distillation proceeds, and it is finished when no more zinc collects in the condenser. The receiver is now removed, and the furnace tilted so as to empty the contents in the liquid state into a slag pot. The residue in the retort is then scraped out, and the furnace brought again into the upright position. Some charcoal powder is thrown in to prevent the oxidation of any lead remaining in the retort, and a fresh charge is introduced, the teeming and filling occupying 20 minutes.

The process lasts 6 to 8 hours; at Omaha, for instance, charges of 9 cwt. are worked off in 8 hours, and the retorts stand 30 to 40 charges, the consumption of coke being on an average 55 per cent. of the weight of the scum. One man attends to 2 to 4 furnaces in each 12-hour shift. Of the entire amount of the zinc in the scum about 75 per cent. is recovered in the metallic state, the remainder being obtained as an oxidised powder, known as blue powder. Of the zinc used in desilverising, from 50 to 60 per cent. is obtained as metal. The blue powder contains 17 to 18 ounces of silver per ton, and is difficult to dispose of, being sent in part to the European zinc works.

The rich lead remaining after the distillation, contains on an average 10 per cent. of silver.

At Cheltenham, St. Louis, the retort charge amounts to 950 lbs., the distillation lasting 8 hours and consuming 450 lbs. of coke; one workman attends to two furnaces.

Stationary furnaces are provided with retorts, tubes or crucibles as distilling vessels, and are heated with coke, coal or gas. In the United States this form of furnace is now rarely used, though

[1] *The Metallurgy of Lead.*

those at Cheltenham, St. Louis, may be mentioned where they are used, together with the Faber du Faur furnace, and the Tatham stationary furnace.

The Cheltenham coal fired furnace is shown in Fig. 345, *a* being the grate, *A* the plumbago retort, *b* the receiver, and *d* the flue. The charge consists of 630 lbs. of rich scum, and the coal consumption amounts to 700 lbs., the distillation lasting 8 to 10 hours. The Tatham furnace fired with coke is used at the Delaware lead works; it is shown in Fig. 346, where *a* is the retort, *b*, *b*, *b* the openings into the flue. The coke is charged from the top, and the ashes removed through the opening *z*. A charge weighs 500 lbs.; the rich lead

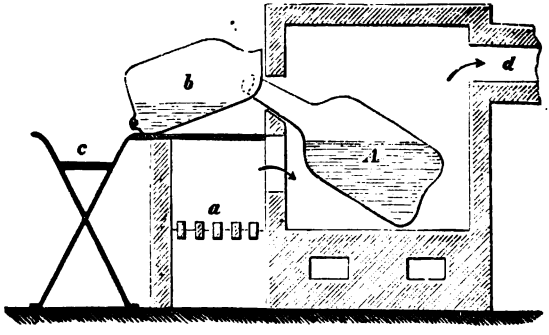


FIG. 345.

after distillation is tapped from the bottom of the retort, the retort residues being scraped out through the neck.

The furnace employed at Port Pirie, South Australia, heated by coal, is shown in Figs. 347–350; *a* is the retort, *b* the grate, and *c* the chimney flue. Four such furnaces are placed side by side, and the charge for each retort amounts to 750 lbs., two charges being worked in 24 hours. The coal consumption runs to about 100 per cent. of the weight of the rich scum, and each retort lasts on an average 30 charges. One workman attends to the four furnaces. The rich lead obtained contains 15 per cent. of silver.

At the majority of continental works, stationary furnaces heated by gas and having tubular distilling vessels are used, (Friedrichshütte Braubach, Ems, Binsfeldhammerhütte and Münsterbach near Stolberg, Hoboken near Antwerp). As many as five retorts may be placed in a furnace, and they are either constructed of graphite, with the requisite amount of clay, or else they are of clay with a clay and carbon lining, the carbon being added as coke, charcoal, coal or graphite (Landsberg's patent). The largest retorts are 2 feet high,

and 2 feet 3½ inches in diameter, and hold 1 ton of zinc scum (Binsfeldhammerhütte). The receivers are either cylindrical, or cylindrical with an enlargement in the middle or skittle-shaped, and last on the average for 30 charges each.

The arrangement of the older furnaces at Friedrichshütte, Upper Silesia, is shown in Figs. 351 to 353, the later furnaces having five

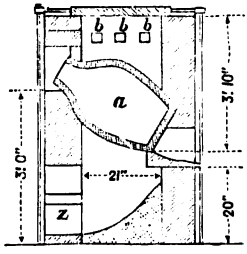


FIG. 346.

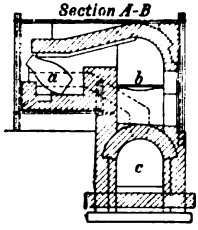
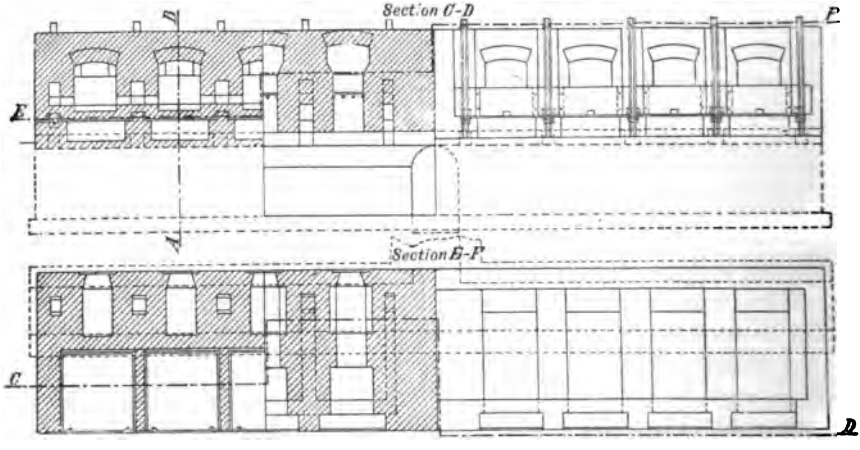


FIG. 347.



FIGS. 348—350.

retorts instead of three. *H* is the gas producer and *R* the heating chamber, the air necessary for combustion entering at *y*, passing through the channels *k*, *k*, and after being heated in this way passing through the slit *v* into the space *w*, where it mixes with the gas. The distilling vessels made of graphite and fireclay are shown at *x*, and *u*, *u* are the receivers for collecting the zinc, the liquid silver-lead alloy remaining after the distillation, being tapped out at *p*. The waste products of combustion pass along the flue *n* to the chimney *J*.

The later form of furnace is very similar but has 5 retorts instead

of 3, each retort holding 5 cwt. of rich scum requiring 12 hours for its distillation. The rich lead is then run out and a charge of 3 cwt. of

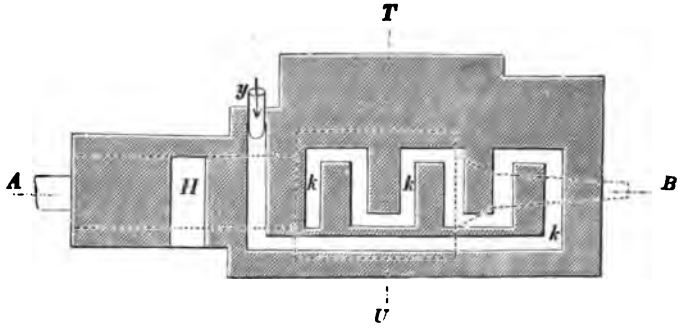


FIG. 351.

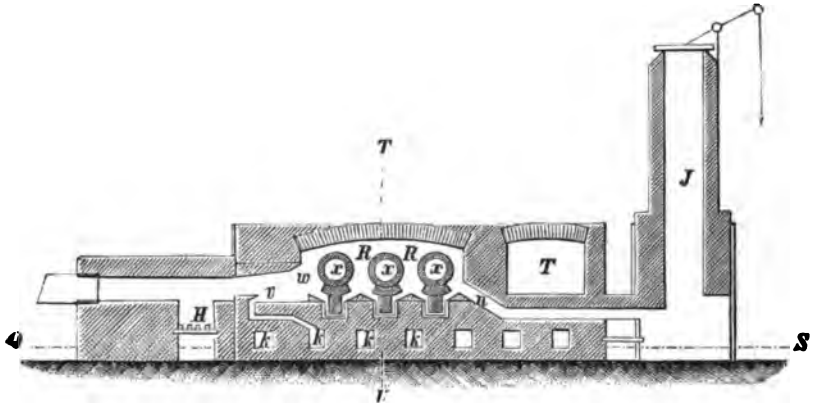


FIG. 352.

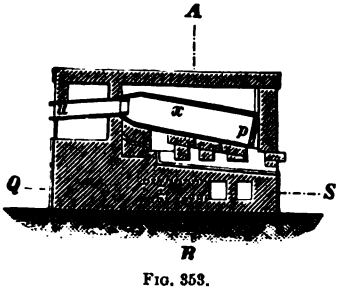


FIG. 353.

rich scum is introduced and distilled for a further period of 22 hours, and the rich lead again tapped off. To the residue now remaining in the retort ½ cwt. of liquated lead containing 0·003 per cent. of silver

from the liquation of the rich scums is added in order to extract the greater part of the silver from the residue, and after a further heating of an hour's duration, the lead, containing now 0·75 per cent. of silver, is tapped off. The lead is added to the residue in the form of small bars weighing ¼ cwt. each. The residue which now remains is smelted with iron refinery slag and lime, yielding a rich lead. A retort lasts on an average 35 charges, 7 retorts being required for the distillation of 100 tons of rich scum. The fuel consumption, including the *cinder* employed as a reducing agent in the retorts, varies from 95 to 100 per cent. of the weight of the rich scum distilled.

At the Friedrichshütte, where lead containing 0·05 to 0·1 per cent. of silver is desilverised, the zinc scums after liquation and distillation leave a rich lead containing 1 per cent of silver. This is again desilverised with zinc, and the scums again distilled after liquation, yielding a rich lead with 7 per cent. of silver, which is then cupelled. In the working year 1892-3 the yield from the liquated rich scum was:—

68	per cent.	Rich lead.
14	„	Zinc.
10	„	Scrapings.

At Braubach there are 2 retorts placed side by side in one furnace. Each retort is charged with 5½ cwt. of rich scum mixed with 1 per cent. of wood charcoal. The distillation lasts from 12 to 13 hours and the products are 60 per cent. of rich lead containing 10 to 12 per cent. of silver and 2 per cent. of zinc, 3 per cent. of skimmings containing 70 per cent. of zinc and 2·0 per cent. of copper, and 35 per cent. of zinc. The yield of zinc is said to be equal to 96 per cent. of the total amount used. The retorts are constructed according to Landsberg's patent and are said to last 150 distillations; the fuel consumption amounts to 60 or 70 per cent. of the weight of the rich scum.

At Hoboken, near Antwerp, where gas furnaces and retorts similar to those of Braubach are in use, every 100 parts of rich scum require 55 to 70 parts of coal and 1 part of charcoal, and yield 11 to 16 per cent. of retort residues. Faber du Faur's tilting furnace has also been experimentally tried but has proved much more costly than the furnace just described. For the same weight of rich scum it consumes double the amount of coke, requires far more retorts and produces more retort residues, so that the advantage of the gas-fired furnace over that heated by coke has been clearly demonstrated.

At Freiberg the rich scums are distilled in plumbago crucibles (Morgan's patent), each placed in a separate circular wind furnace 31

inches across and 36 inches deep to the grate level. The furnace is charged from the top after removing the fireclay cover. The plumbago crucible $15\frac{3}{4}$ inches across at the top, $21\frac{3}{4}$ inches high and 2 inches thick, is provided with a plumbago cover 8 inches high, and with a plumbago delivery tube 20 inches long, $3\frac{1}{8}$ inches wide and 1 inch thick in the walls. This exit tube opens into an iron box $19\frac{1}{2}$ inches high, 7 inches wide at the top and 10 inches wide at the bottom, in which the zinc vapours condense.

The arrangement of the furnace with crucible and receiver is shown in Fig. 354, where t is the crucible with cover v, E the heating chamber, x the grate, m the exit tube for the zinc

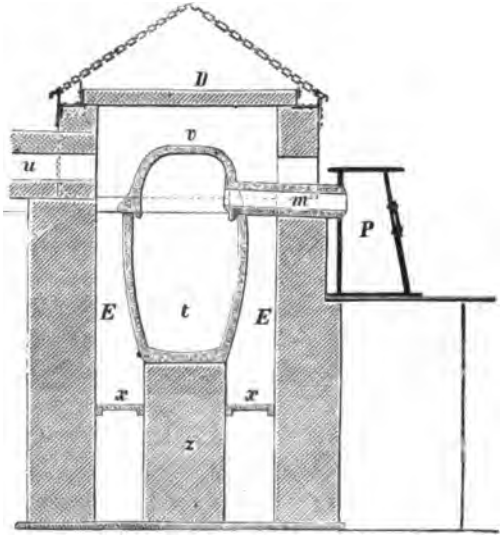


FIG. 354.

vapour, and P the receiver. The crucible rests on the stand z, and can be lifted out after removing the cover D. Coke is used as fuel, and is packed round the crucible, resting on the grate x, and the waste products of combustion pass out into the chimney by the flue u.

The zinc scum is mixed with 1 per cent. of coarse charcoal powder and charged into the crucible after the bottom of the latter has been covered with a layer of pieces of charcoal, $4\frac{1}{2}$ cwt. of scum constituting a charge. After the hood has been luted on, the space between the crucible and the furnace walls is filled with pieces of coke of the size of walnuts or hen's eggs, and then up to half the height of the hood with glowing coke and the cover of the furnace is placed in position. As soon as the carbon monoxide flame is seen at

the end of the exit pipe, the condenser cover is fastened on and the zinc collects in a lump in the receiver. The distillation lasts 8 to 9 hours, and from 100 parts of rich scum the following products are obtained :—

57·17 per cent. rich lead containing 0·0186 per cent. of gold and 7·35 per cent. of silver.
5·85 per cent. of residues containing 0·112 per cent. of gold, 4·608 per cent. of silver and 3·5 per cent. of copper.
29·54 per cent. metallic zinc.
6·35 per cent. zinc in the form of zinc dust and scrapings (7·22 per cent.).

90·4 per cent. of the zinc content of the rich scum is recovered, that is, 50 per cent. of the zinc used in desilverising. The consumption of fuel amounts to 376 to 440 lbs. of coke for 2 to 2½ cwt. of rich scum, and one crucible lasts for 80 charges.

At Bagilt, in Flintshire, plumbago crucibles are also in use for the distillation of zinc from the rich scums. Each crucible holds 540 to 628 lbs. of rich scum, and the distillation lasts 8 hours, 352 lbs. of the best coke being used for each charge; 15 per cent. of the weight of the rich scum in zinc is recovered, that is, 45 per cent. of the zinc used for desilverising. The retort residues amount to 15 per cent. of the weight of the charge and they are smelted with rich litharge in reverberatory furnaces.

Every 1,000 tons of rich scum require 94·6 crucibles (costing £5 each), the coke used for this quantity being 625 tons, the distillation in crucibles with coke being more costly than the employment of gaseous fuel.

Rösing has suggested distilling the zinc from the rich scum by the aid of intensely heated molten pig iron, the high temperature of which would cause the zinc to distill off, the argentiferous lead collecting below the molten metal. The process is to be conducted in basic lined vessels placed in a tilting furnace, and by tilting the furnace the iron would flow out first and could be employed again, and the rich lead would follow. Up to the present this process has not come into use.

As zinc boils in a vacuum at a much lower temperature than at the ordinary pressure, the question suggests itself as to whether suitable apparatus could not be devised for effecting the distillation under reduced pressure.

2. Smelting Rich Scum with Ferruginous Slags in the Blast Furnace

By smelting the rich scum in this way it is possible to slag off the greater part of the zinc, and to volatilise the remainder, and thus to

obtain a rich silver-lead alloy. By using a low blast pressure the volatilisation of lead and silver can be greatly diminished.

This process was devised by Flach and Siéger, and is known as the Flach process, and in the case of scums rich in zinc is attended with considerable loss of silver through volatilisation and loss in the slag. These losses are the smaller, the higher the lead content of the zinc scums in proportion to the zinc present, but in this case the resulting rich lead will be poorer in silver, giving rise to greater losses in cupellation.

Even with scums rich in lead the resulting slags cannot be rejected as worthless, but must be further smelted in order to recover the silver they contain. The high zinc content of these slags renders the smelting difficult and costly, and leads to further losses of silver in the slags and by volatilisation.

In this process the zinc is completely lost, though the method is simple and cheap, and was largely used on these grounds, but on account of the disadvantages mentioned it has been replaced by the distillation process in most works.

As long as the price of zinc remains so high that the cost of distillation is covered by the zinc recovered, and, provided that the silver losses in both processes are about equal, the distillation process will continue to retain the advantage over Flach's method.

3. Cupellation of the Rich Scums

The separation of zinc from the rich scums by an oxidising melting with additions of litharge, is attended with a high loss of silver. In addition to this, skimmings rich in silver and zinc are produced which need subsequent treatment in blast furnaces, this after-treatment being in its turn attended with considerable loss of silver. The process was formerly carried on in some places in cupellation hearths, in combination at times with cupellation of the lead, but is not now in use, as not only was the loss of silver great, but the whole of the zinc was also lost.

4. Melting Zinc Scums with Alkaline Chlorides

The object of this process was to convert the zinc into chloride by the action of molten alkaline chlorides. It was formerly in use in some continental works, but is now entirely abandoned, as it was costly and troublesome, and the zinc, not volatilised as chloride, formed a worthless slag containing the same compound.

5. The Oxidation of the Zinc by Steam

In this process the rich scum is converted into a mixture of zinc oxide, lead oxide, and rich silver-lead by the action upon it of steam under pressure. From this mixture the zinc oxide may be dissolved out by means of acids or by a solution of ammonium carbonate, and the zinc obtained as basic carbonate, oxide or sulphate.

This process gives the largest yield of silver of any of the methods of treating the scum, but it is complicated and costly, and can only be used when the zinc bye-products can be disposed of at high prices. If the price of metallic zinc is high as compared with that obtained for zinc products, the distillation process is preferable.

The process demands a scum rich in lead and consequently poor in silver, as otherwise, owing to its difficult fusibility its decomposition by steam is incomplete.

The method of treating the zinc scum by means of steam was suggested by Cordurié and first used at Rothschild's works near Havre; it is therefore known as the Cordurié process.

The process consists in passing steam at 1½ to 5 atmospheres pressure into the red-hot molten alloy contained in cast iron or cast steel pots provided with hoods and exit tubes.

The zinc contained in the red-hot alloy decomposes the steam into its elements, the zinc combining with the oxygen forming zinc oxide. and hydrogen being liberated. As during the melting of the alloy and also during the decomposition, air cannot be altogether excluded (there must be no back pressure of gas above the bath of metal,. otherwise explosions would be caused by the hydrogen), a considerable amount of the lead is oxidised as well as zinc, and a mixture of lead and zinc oxides is obtained. This mixture, which is at first entangled amongst the molten lead, but separates after a time, forms a loose greyish-green powder on the surface of the bath. The undecomposed lead collects at the bottom of the vessel, the greater part of the lead having already liquated out during the melting of the scum, though a portion of it remains entangled in the form of small shots in the oxides formed. Copper and antimony are partly oxidised by the air present and partly remain behind with the lead.

The products of the operation are, then, a metallic portion consisting of the lead-silver alloy, and an oxidised portion consisting of a mixture of zinc and lead oxides containing all the zinc present originally in the scum, entangling some portions of the metallic product and forming a powdery mass lying above the metallic portion.

At Lautenthal and Altenau where rich scums, the composition of which has previously been stated (page 537), are subjected to this process, the metallic portion contains 2 to 4 per cent. of silver and the oxidised portion 1 to 2 per cent., the detailed composition of the two products at both works, according to Rösing, being as follows:—

Metallic Portion.

	Altenau.	Lautenthal.
Lead	96·3448	95·1404
Zinc	0·0027	0·0023
Copper	0·8279	0·4645
Silver	2·41	3·65
Bismuth	0·0142	0·0169
Antimony	0·3914	0·7201
Iron	0·0054	0·0044
Cadmium	traces	traces
Nickel	0·0036	0·0014

Oxidised Portion.

	Altenau.	Lautenthal.
Lead	37·845	30·065
Lead oxide	32·14	36·87
Zinc	1·35	1·9
Zinc oxide	23·37	23·24
Copper	1·12	1·24
Silver	1·245	1·855
Bismuth oxide (Bi_2O_3)	0·43	0·44
Antimony oxide (Sb_2O_3)	1·06	0·57
Arsenious oxide	traces	
Ferric oxide	1·44	3·82
Cadmium, Nickel	traces	traces

At Lautenthal a portion of the rich scum is melted in charges of 10 tons in a cast iron pot furnished with a hood of iron plate. The pot is arranged similarly to that figured on pages 439–441, Figs. 277 to 279, and used for lead softening. The melting proceeds only slowly on account of the zinc and the oxides present, and after 8 hours the rich scum is found in a semi-molten condition and at a red heat. Steam at two atmospheres pressure is now admitted at the bottom, and acts energetically upon the zinc, which is completely oxidised at the end of 4 hours, the completion of the process being indicated when a sample withdrawn from the pot ceases to show any zinc flame.

As a certain amount of argentiferous flue dust is carried over by the steam, the vapours from the pot must be conducted through a condenser made as long as possible in order that the flue dust may be deposited. At intervals the condenser must be provided with exit valves opening outwards and furnished with hydraulic lutes in order to afford a means of relief in case of explosion of the hydrogen and air. Such explosions are easily caused if the pressure in the hood above the bath of metal is increased, and the gases collecting there must be drawn off as quickly as possible by maintaining a good draught which may be effected by means of a steam jet.

The flue dust collected at Lautenthal has the following composition :—

Zinc oxide . . .	69·6	Arsenic	trace
Zinc	0·12	Antimony	0·17
Lead oxide . .	28·2	Ferric oxide . . .	0·34
Lead	0·71	Alumina	0·24
Silver	0·03	Insoluble residue .	0·42
Copper	0·17		

This flue dust is extracted with acids with the object of recovering the silver, the latter remaining in the insoluble residue.

Each pot lasts for about 12 charges, and from every 100 parts of rich scum about 50 to 54 parts of rich lead and 46 to 50 parts of oxide are obtained. The coal consumed is about 13 per cent. by weight of the rich scum, 9 per cent. being used for heating the pot and 4 per cent. for the generation of steam, and one workman is required for each pot. The rich lead produced is cupelled, whilst the mixture of oxides, after being deprived of the zinc contained in it, is added to the rich lead in the cupellation process.

The Lixiviation of the Oxides Produced in Dezincising

The oxidised portion was formerly added directly to the cupellation of the rich lead without any previous separation of the zinc. In this case it was not possible to get the entire silver content of the oxides completely into the rich lead, and the zinciferous oxides left after the cupellation still contained 0·4 per cent. of silver. These oxides were smelted with a rich lead flux (litharge) producing argentiferous lead, or else they were smelted with argentiferous galena.

In both cases, loss of silver in the slag was unavoidable, and these processes were replaced by the one now employed, in which the mixture of oxides is first extracted with acids in order to dissolve out

the zinc contained in it. The lixiviated oxide can then be added to the rich lead cupellation, its content of silver uniting with the silver of the rich lead, and the litharge it contains mixing with the litharge produced in the cupellation.

The best solvents for the zinc oxide are ammonium carbonate and sulphuric acid, and as sulphuric acid is cheap and produces a marketable salt, viz., zinc sulphate, it has, on account of its simplicity and the ease with which the acid dissolves the oxide, a distinct advantage over the ammonium carbonate process, now to be considered.

The Extraction of Zinc Oxide by means of Ammonium Carbonate

This process, which was suggested by the author,[1] depends upon the easy solubility of zinc oxide in ammonium carbonate solution, and upon the fact that from this solution, ammonia and a part of the carbon dioxide may be recovered by boiling, whilst zinc carbonate is precipitated and may be converted into the oxide by ignition. The solvent power of the ammoniacal solution is restored to it by passing into it the carbon dioxide given off on heating the basic carbonate.

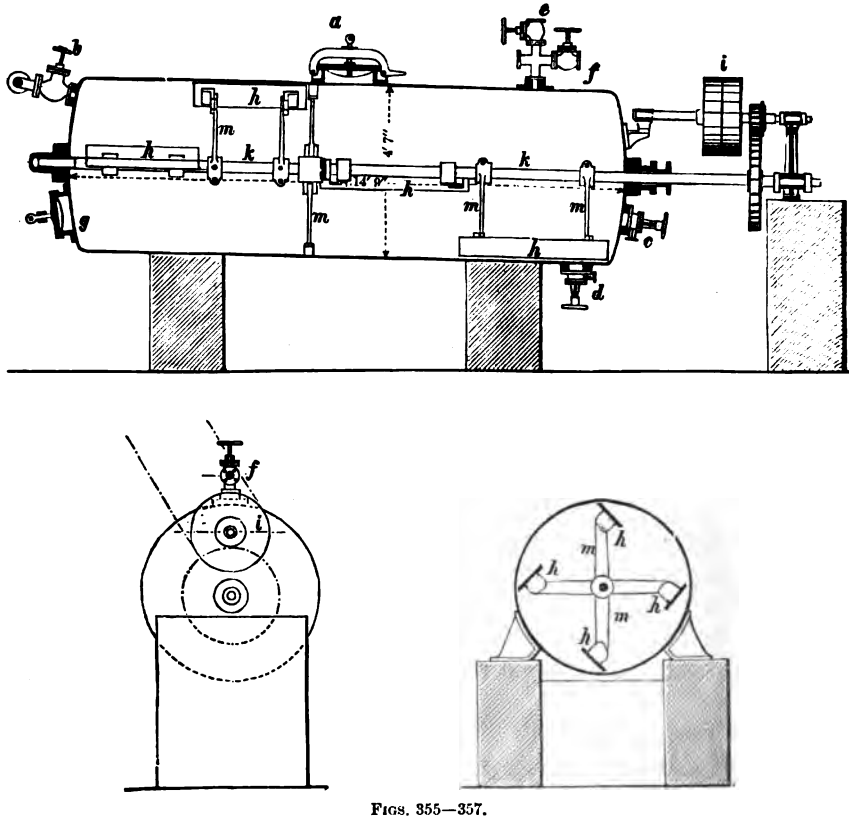
This process was first used at the Lautenthal works but was afterwards superseded by the process of extraction with sulphuric acid. At present (1894) it is in use at the Hoboken works near Antwerp, but will cease to be worked there when the aluminium-zinc desilverising process is introduced.

In this process the mixture of oxides is treated in horizontal wrought iron cylinders in quantities of 1 to 1½ tons for 12 hours with a solution containing 9 per cent. of ammonia and 9 per cent. of carbon dioxide.

The arrangement of the dissolving vessel is shown in Figs. 355 to 357, where *a* is the opening provided with a cover made tight by an india-rubber washer for the introduction of the oxide, *b* is a pipe provided with a valve for admitting the ammoniacal solution; *c* and *d* are openings also furnished with valves, for running off the zinc solution; *g* is a manhole for removing the residue; *f* is a pipe for the introduction of wash water, and *e* is a pipe for the admission or exit of air. The agitating apparatus consists of an axle *k* provided with arms *m*, these in their turn carrying the paddles *h*; the axle and arms are of wrought iron and the paddles of cast iron, and the agitator is worked by the pulley *i*. After solution is complete,

[1] *Preuss. Minist. Zeitschr. für Berg. Hütten. und Salinenwesen*, vol. xxviii., 1880.

the bulk of the contents of the vessel, both the liquid portion and the suspended solid part and slime, are run into a pressure vessel (montejus) of cast or wrought iron, whence it is forced by compressed air into a filter-press, where the liquid portion is separated from the solid. The solid portion, together with the solid residue remaining in the solution vessel, and consisting chiefly of small grains of lead, is treated in cast iron vessels with steam at 5 atmospheres pressure,



FIGS. 355—357.

the last portions of the ammonia being in this way driven off and rendered available for future operations.

In this way a dry solid residue of oxide free from ammonia and containing 2 to 3 per cent. of silver is obtained, and this is added to the rich lead on the hearth of the German cupellation furnace.

The liquid obtained by filtration contains the zinc oxide dissolved in ammonium carbonate solution, and on boiling yields its zinc as a mixture of hydroxide and basic carbonate, forming a snow-

white powder suspended in water, ammonia gas and carbon dioxide being given off at the same time.

If the zinc scum was cupriferous, the oxidised portion will contain copper oxide, which is also soluble in ammonium carbonate solution, and on boiling, the copper separates as oxide and colours the basic zinc carbonate grey. This discolouration can be prevented and the copper recovered by precipitation with metallic zinc before boiling the solution, the zinc dissolving and precipitating an equivalent amount of copper.

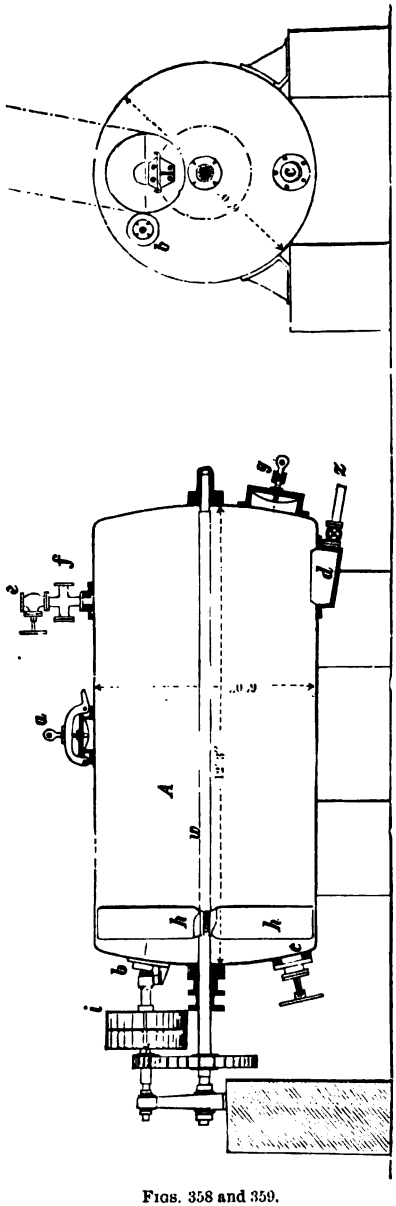
The liquid, after separation from the oxide by means of the filter press, is run into a wrought iron precipitating vessel, where, by means of an agitator, it is brought into intimate contact with zinc. Such a vessel is shown in Figs. 358 and 359, *A* being the precipitating vessel, *e* the pipe for the introduction of the liquid, and *a* an opening, made tight with a rubber washer, and serving for the introduction of the zinc; the stirrers, *h*, *h* are affixed to the horizontal axle *w*. The precipitated copper collects at the bottom of the vessel and is withdrawn through the manhole *g*. The liquid freed from copper is run off through *c*, and the final portions through *z*. Wash water is introduced at *f*.

The boiling of the ammoniacal zinc solution for the purpose of recovering the ammonia and precipitating the zinc, is carried out in vertical cylinders of boiler plate with conical lower ends, into which steam at 5 atmospheres pressure can be introduced. Direct firing cannot be used, as the zinc carbonate would collect on the sides and bottom of the vessel and form a crust. The use of steam also accelerates the process, as the liberated ammonia and carbon dioxide are carried off by it as it bubbles through the liquid. The distillation lasts 12 to 15 hours.

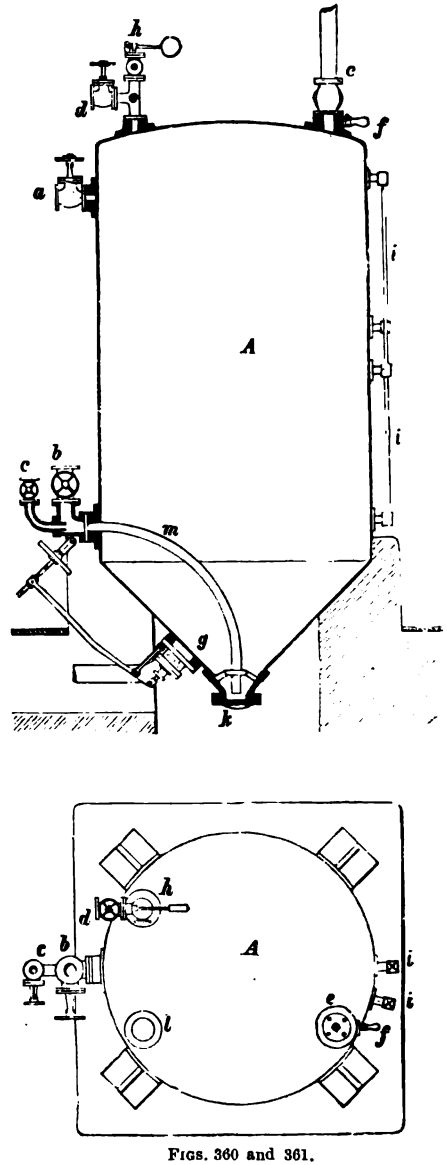
The arrangement of this distillation vessel is shown in Figs. 360 and 361, the zinc solution being introduced through the tube *a*, whilst exhaust steam from an engine is admitted through the valve *c*, passing by the pipe *m* to the bottom of the vessel; and in case this is not sufficient, steam can be admitted direct from the boiler by means of the valve *b*. The liquid is thus raised to the boiling point, and the evolved ammonia and carbon dioxide pass together with the steam through the pipe *e* to the dephlegmator and condenser, the basic zinc carbonate being precipitated in the vessel. As it falls on the conical bottom of the vessel it comes continually into contact with the entering steam, and thus gives up its ammonia completely.

After the ammonia is evolved, only water and the precipitate are left in the vessel, and they are drawn off together by closing *e*, con-

tinuing the admission of steam through m and opening g, the steam



FIGS. 358 and 359.

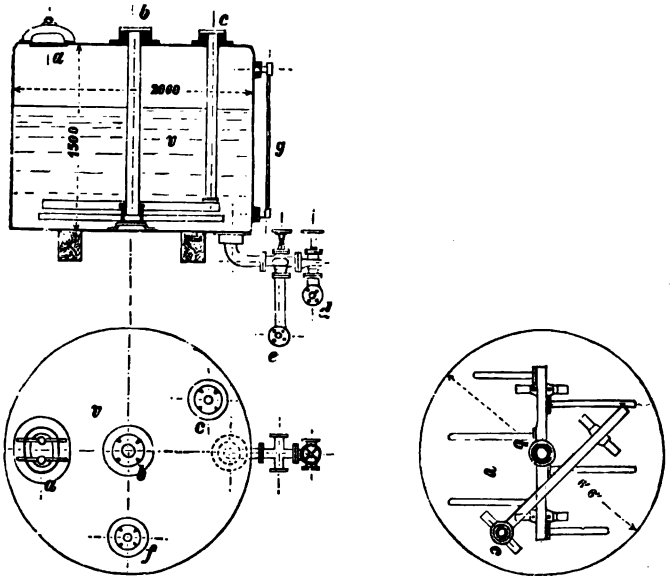


FIGS. 360 and 361.

pressure thus driving the contents through the latter opening. The mass is either run into a wooden box, and the precipitate allowed

to settle in the box, or it is transferred from the box to a filter press, or else the mass is directly filter-pressed. This takes some time, and diminishes, in consequence, the capacity of the apparatus which would have otherwise been charged with a fresh quantity of ammoniacal zinc solution.

The gases evolved from the still are condensed in a series of Woulf's bottles of wrought iron, containing dilute ammonium carbonate solution, part of which is obtained by washing the residue and part collected in the dephlegmator. The ammonia and carbon dioxide evolved from the still are largely diluted with steam, and, before



FIGS. 362—364.

entering the condensing arrangement proper, must be deprived of part of this. This is effected by means of a dephlegmator, in which the gases, before entering the condenser, are led through a wide sloping tube, kept cool by water on the outside, the greater part of the steam condensing, whilst the gaseous ammonia and carbon dioxide pass on. This is effected by so regulating the amount of out-flowing and in-flowing water that the temperature is maintained between 60° and 70° C. The condensed water flows from the sloping bottom of the dephlegmator tube, carrying with it a small quantity of ammonia, and is either used as wash-water for the distillation residue or else as an absorbent in the Woulf's bottles.

In order to replace the carbon dioxide which is used up in producing the basic zinc carbonate, carbon dioxide is forced under pressure into the first Woulf's bottle, the impure gas from burning coke being used for this purpose. The coke is burnt in a small shaft furnace, provided with a grate, and the evolved gas is drawn off by the force pump. The arrangement of the Woulf's bottles, of which there are three or four joined in series, is shown in Figs. 362, 363 and 364. They are wrought-iron cylinders *v*, into which the ammonia, carbon dioxide and some still uncondensed steam enter by the pipe *b*, the unabsorbed gas passing through *f* into a second condenser. Through the pipe *c*, carbon dioxide is passed in order to convert the excess of ammonia into ammonium carbonate. The contents are drawn off at *e*; *g* is a water gauge, and *a* a manhole.

The arrangement of the new plant at the Hoboken works, near Antwerp, is shown in Figs. 365 and 366, where *f*, *f* are the solution vessels, and the ammoniacal zinc solution runs from them into the pressure vessel *y*, from which the solution with its suspended solid matter is forced by means of compressed air into the filter presses *e*, *e*. From the latter it passes, if free from copper, into the pressure vessel *z*, and thence into the retort *g*, or, if it contains copper, then it is forced from the filter press into the precipitating tank, *d*. After extracting the copper, the liquid is run into the pressure vessel *z*, and from there forced by compressed air into the still *g*. The gases given off from the latter during distillation pass along the pipe *r* into the dephlegmator *b*, the wrought-iron water jacket for which is not shown in the drawing, and the liquid collected here flows into the reservoir *h*, from which it is taken to serve either as the absorbing liquid in the Woulf's bottles, or as wash-water for the residue. The gases pass along the pipe *u* into the first condenser, *c*, and the gases from this into c^1 and c^2, the exit gas from the latter, consisting chiefly of carbon monoxide and nitrogen from the coke furnaces gases, being either allowed to pass into the air, or else being passed through sulphuric acid in an open vessel, for the purpose of condensing any ammonia carried over. The ammonium carbonate liquor in the condensers is drawn off by connecting pipes into the solution vessel, where its solvent powers are again utilised. *a* is a water tank, *o* is the carbon dioxide forcing pump, *k* the air compressor, and *w* the engine for forcing water up into the reservoir. From the latter the water flows into the dephlegmator box and the cooling pipes for the condensers. The space *k* is occupied by the small shaft furnace for generating the carbon dioxide.

The loss of ammonia in the process is very slight. The basic zinc

carbonate which is precipitated is converted into zinc oxide by heating to redness in reverberatory furnaces. The zinc oxide so produced is inferior in covering power to that made by burning the metal, and it

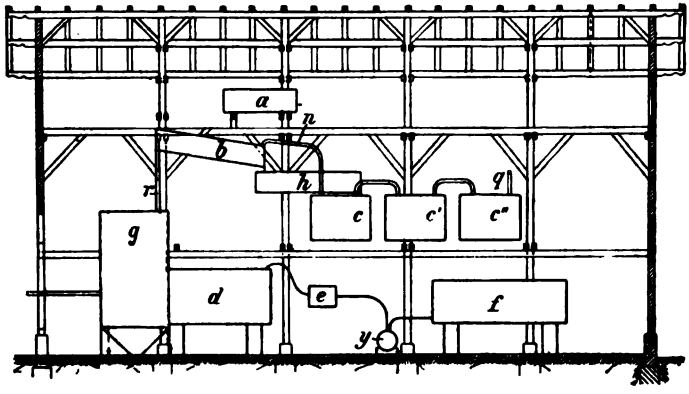


FIG. 365.

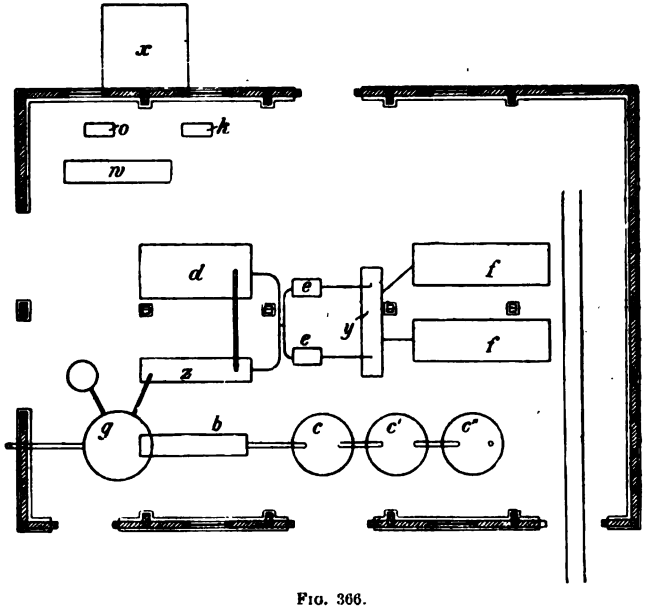


FIG. 366.

has also a faint yellow tinge, so that it cannot be sold at the price obtained for zinc white. On this account it is sold to the zinc chloride makers, and if the works happen to be situated near to the smelting works, the basic carbonate may be sold to the latter direct.

Each ton of oxide consumes from 1 to 1·25 tons of coal for solution, precipitation, distillation, &c., and to prepare 1 ton of oxide from the basic carbonate 1¼ to 1½ tons of coal are required.

The yield of silver amounts to 1½ to 2 per cent. more than indicated by the assay.

The whole process is complicated, requiring costly plant and expert attendance, and the zinc is obtained in a form in which it sells for less than metallic zinc, though there is the advantage that the silver yield is high.

The possibility of employing the process depends mainly upon low price of coal and the disposal of the basic carbonate at a fairly high price.

Owing to the progress made with the distillation process of treating the rich scum subsequently to the introduction of this ammonia process in 1878, the former method has the advantage over the latter in spite of its higher yield of silver.

The Extraction of the Zinc Oxide with Sulphuric Acid

This process was introduced by Pfort at the Lautenthal works, and is a much simpler method than the one just considered. It can only, however, be used where sulphuric acid can be obtained cheaply, and where a market can be found for the zinc sulphate produced, —conditions which at that time prevailed at Lautenthal.

Dilute sulphuric acid will dissolve out zinc from the mixture of oxides without attacking the lead oxide or the silver, and it also dissolves zinc from any undecomposed zinc scum which may be present. At Lautenthal (the only works where this process is used) the solution of the zinc oxide is effected in lead-lined wooden vats with sloping bottoms, the sulphuric acid being allowed to act so long as it dissolves zinc or zinc oxide. The solution of zinc sulphate is allowed to settle, evaporated in pans to the crystallising point, and then run into crystallising vats. The remaining residue is washed, dried, and added to the rich lead on the cupellation hearth.

The Working up of the Dezincised Oxide

The oxide, deprived of its zinc by either the ammonia or the sulphuric acid process, is treated in each case in the same way. As soon as the bath of rich lead on the hearth of a German cupellation furnace has been deprived of its impurities, that is, when yellow litharge begins to form, the oxide is added by degrees after interrupting the blast. After each addition the molten lead oxide on the surface of the bath is removed, and when the whole has been

added the cupellation is conducted as usual. The scum raked off from the surface of the bath (*abzug*) contained 0·06 per cent. of silver when the author was at Lautenthal, and was added to the ore smelting charge. When the oxide was added directly to the bath without previous extraction of the zinc, the *abzug* contained 0·3 per cent. of silver, and the whole of the zinc content of the oxides.

The combined Pattinson and Zinc Desilverising Processes

The two processes are only combined with the object of separating the bismuth present in the work-lead, and the only place where this is carried out is at the Muldener Hütte at Freiberg. The lead at these works, after undergoing the liquation and refining processes, contains 0·4 to 0·8 per cent. of silver, and is submitted to the Pattinson process, and enriched up to 2 per cent. of silver, the rich lead carrying with it the bismuth. This rich lead is then cupelled, and the litharge produced, which is rich in bismuth, is worked up for that metal and for lead. The poor lead free from bismuth is treated by the zinc process to further desilverise it.

There are nine pots in the Pattinson battery, the work-lead being charged into the third or fourth, and withdrawn from the first with 2 per cent. of silver, the poorer lead from the eighth or ninth pot containing 0·1 per cent. of silver, and it is this poor lead which is desilverised by zinc. The desilverising is conducted in cast-iron pots, the zinc scums are liquated in small pots of the same material, and then distilled in plumbago crucibles, whilst the poor lead is deprived of its zinc by oxidation in a reverberatory furnace. Details of these processes have already been given.

Silver and Lead Losses in the Zinc Process

With careful working, the loss of lead should not amount to more than 1 to 2 per cent., the loss of silver depending on the mode of treatment of the rich scums. If the distillation method is used, the yield of silver should be that given by assay, whilst, using the method of dezincising by steam and dissolving the zinc oxide, the assay figure should be exceeded (without including the smelting remedy) by 2 per cent., giving a yield of 102 per cent.

The Production of a Zinc-Silver Alloy from Work-Lead

The researches of Roessler and Edelmann have shown that it is possible to obtain the greater part of the silver content of work-lead in the form of a zinc-silver alloy.

o o

If in desilverising by means of zinc, the oxidation of the bath of metal can be prevented, a zinc scum, rich in silver and zinc, is produced from which the adherent lead can be separated for the most part by liquation. To obtain such a zinc scum free from oxide it is necessary to add a small proportion (0·5 per cent.) of aluminium to the zinc used for desilverising, the aluminium preventing the oxidation of the zinc and lead. It is only efficacious however in this respect when the work-lead is free from copper and arsenic, and both these bodies, if present, must be removed before desilverising. If copper is only present in small amounts, it may be removed by the addition of a small quantity of zinc to the bath of molten metal. Antimony, as in the ordinary zinc process, is only harmful if present in considerable amount.

According to Roessler and Edelmann's researches the action of aluminium is prevented by the presence of 0·1 per cent. of copper, oxidation then taking place ; 0·05 per cent. of arsenic acts similarly, whilst 0·03 per cent. of antimony has no injurious influence, thoguh the presence of 1 per cent. of antimony renders the desilverising very imperfect and necessitates the use of a large amount of zinc.

The following description is given by the authors of the process :—

"1. If 22 lbs. of zinc containing 0·5 per cent. of aluminium are added to 220 lbs. of lead containing 5⅓ ozs. of silver and the mixture be stirred and heated to 500°C., about 3·3 lbs. of zinc will dissolve in the lead, whilst the remaining 18·5 lbs. separate out, and carry, dissolved, almost the whole of the silver. If in order to separate this argentiferous zinc, the mass be allowed to cool to 450°C. about 11 lbs. of zinc will collect on the surface in the fluid state, and if the temperature is eventually lowered to 350° then a metallic scum forms on the surface, containing about 9 lbs. of zinc and the last portions of the silver.

"2. To 220 lbs. of lead with the same amount of silver only 3·3 lbs. of aluminiferous zinc (½ per cent. Al) were added, the zinc being spread on the surface, and thoroughly dissolved in the lead by raising the temperature to 500°C. and carefully stirring the mass. If now it be allowed to cool gradually, no zinc separates out in the molten state, but a silver-zinc alloy rich in silver and infusible at this temperature forms on the surface as a pasty mass, being mixed with lead and forming about 10 per cent. by weight of the entire charge, containing all the silver and being easily separable from the desilverised lead below it. If the cooling is conducted very slowly, the sides of the vessel being often scraped, the desilverising is very complete, and it will be found that the first scum weighing about 9 lbs. is very rich in

zinc and silver, whilst the portion collecting later on and weighing about 13 lbs. consists almost entirely of lead and contains little silver or zinc.

"3. The 9 lbs. of first dross can be heated at once in an iron pot to low redness (about 650° C.), yielding a rich zinc-silver alloy and a liquated lead containing some silver. If the liquated lead and the other scum be added to the next lot of metal to be desilverised, then at each operation the entire silver content of the lead is obtained, alloyed with half the zinc, the other half of the zinc remaining in the poor lead. The alloy contains 20 to 25 per cent. of silver."

These observations only hold good in the case of pure lead. With commercial leads, the presence of copper and arsenic, as already mentioned, interferes with the action of the aluminium, and large amounts of antimony are also injurious. These bodies must consequently be removed before desilverising, small amounts of copper and arsenic being got rid of by stirring a little zinc into the molten bath. The inventors further state:—

"4. 220 lbs. of lead containing 0·15 per cent. of silver, 0·3 per cent. of antimony, 0·1 per cent. of copper, and 0·05 per cent. of arsenic were purified by using 0·2 per cent. of zinc, very little silver being extracted, and the amount of copper and arsenic being reduced to one quarter. The desilverising was then proceeded with, with excellent results, using 1·2 per cent. of zinc, and about 11 lbs. of rich scum were obtained, capable of being separated into $1\frac{1}{2}$ lbs. of alloy and $9\frac{1}{2}$ lbs. of liquated lead and also about $15\frac{1}{2}$ lbs. of second scum, the lead being desilverised down to 0·07 to 0·11 ozs. per ton.

"5. Lead containing 0·3 per cent. of silver required 1·4 per cent. of zinc for desilverising, with 0·5 per cent. it required 1·6 per cent. of zinc, and with 0·7 per cent., 1·8 per cent. of zinc.

"The alloys weighed 2·6 to $5\frac{1}{2}$ lbs. and contained 25 to 35 per cent. of silver. The principal scum weighed 22 to 33 lbs., the second one $15\frac{1}{2}$ lbs., and the liquated lead $17\frac{1}{2}$ to $26\frac{1}{2}$ lbs. In order to dissolve up all the zinc the temperature at the beginning in these cases had to be raised to 550° to 600° C."

Very little more zinc is thus required, when aluminium is used, than in the ordinary zinc process of desilverising. In conducting the process on the large scale, it is not possible to convert the entire silver content of the work-lead into a zinc-silver alloy, a certain amount of it being retained by the oxides formed during the liquation of the alloy. In separating a small amount of copper by means of a preliminary addition of zinc, a certain amount of silver also goes into the so-called copper scums. It is, consequently,

always necessary to treat these bye products containing zinc, silver and lead, or copper, zinc, silver and lead, by one of the methods previously described for the treatment of the rich scums, viz., the distillation process, the Flach process, or by decomposition with steam and subsequent treatment either with ammonium carbonate solution or sulphuric acid. The amounts of oxidised products and of liquated lead are also greater when the process is worked on the large scale than is indicated by the figures just given.

At present (1894) the process is in use at Hoboken near Antwerp and at Lautenthal in the Harz.

At Hoboken, where work-lead from various countries is desilverised, the zinc is first alloyed with aluminium and then added to the lead previously freed from impurities, the stirring being done in the same way as in the ordinary zinc process. Two argentiferous alloys are obtained, the first scum a rich silver-zinc alloy called "cream" (*rahm*) and the second scum (*hauptabhub*) very rich in lead and containing the remainder of the silver.

The *rahm* constitutes from 1 to 5 per cent. by weight of the work-lead according to its silver content, and the *hauptabhub* 5 to 9 per cent. The consumption of zinc varies from 1·7 to 2·8 per cent. of the weight of the work-lead according to the degree of purity of the work-lead and its content of silver. The consumption of coal, including that used for refining the desilverised lead in the pots, amounts to about 12 per cent. of the weight of the work-lead.

Both the scums are melted together and liquated in cast-iron pots similar to those used in the liquation of the zinc scums, a zinc-silver alloy, dross and liquated lead being the products. From 100 parts of a mixture of the two scums liquated together in quantities proportionate to the amounts in which they were produced in desilverising, from 9·7 to 13 per cent. of zinc-silver alloy would be obtained, 8·7 to 12·5 per cent. of dross and 76 to 77 per cent. of liquated lead, the fuel used being from 8 to 10 per cent.

The zinc-silver alloy is either treated electrolytically or else treated with sulphuric acid and the zinc converted into sulphate. The dross is distilled in retorts, and the liquated lead goes back to the desilverising operation. From 78 to 80 per cent. of the entire silver content of the work-lead is converted into the zinc-silver alloy.

The following are the results of more extended working at Hoboken with Spanish lead containing 49 ozs. of silver per ton. The total consumption of zinc amounted to 1·42 per cent. of the weight of the work-lead. Of this, 0·29 per cent. was used unalloyed with aluminium, for the purpose of extracting the copper and

gold in the lead, the remainder being alloyed with 0·5 per cent. of aluminium and used for desilverising. The first rich scum (*rahm*) formed 1·5 per cent. of the weight of the work-lead and the second scum 4·6 per cent. By liquating this second scum, in addition to liquated lead, 9·8 per cent. of a zinc-silver alloy containing 20 per cent. of silver and 4 per cent. of lead was obtained and 2·5 per cent. of dross, whilst from the liquation of the *rahm* 4 per cent. of alloy with 12 per cent. of silver and 4 per cent. of lead, 34 per cent. of dross and liquated lead were obtained. By the term dross is meant the oxidised crust separating out during the liquation of the alloy.

The following are the products from a hundred parts of work-lead :—

90·7	parts	refined lead
1·4	„	liquated scum
2·9	„	copper scum
3·9	„	*abstrich*
0·7	„	lead dross
0·6	„	alloys
0·7	„	dross rich in silver.

And the silver contained in the lead is distributed as follows:—

1·3	per cent.	in	the	liquated scum
9·9	„	„	„	copper scum
78·9	„	„	„	zinc-silver alloys
9·9	„	„	„	dross.

In the desilverising of rich Australian work-lead from Broken Hill, alloys with 30 to 35 per cent. of silver were produced.

This still modern process has the advantage of obtaining by far the greater part of the silver as a zinc-silver alloy which can be treated electrolytically, thus avoiding the costly cupellation process with its attendant loss of silver. The amount of the bye-products is very small and the direct yield of market lead is very high. The favourable returns given above are the result of several years' working at Hoboken, where the zinc-silver alloys are treated both by electrolytic methods and by treatment with sulphuric acid. In the latter case the alloy is granulated and treated with the acid in lead towers, a silver slime being obtained which can readily be fused. The electrolytic process does not seem to possess any advantage over this method of separation.

The method which has answered best hitherto has been to use cathodes of sheet zinc in the form of circular discs, which can be

rotated on their axes in such a way that half of the disc is exposed and the other half immersed in the solution.

It seems likely that this process of desilverising with zinc containing aluminium will be introduced into other smelting works.

The Cupellation of Argentiferous Lead

The cupellation of argentiferous lead consists of an oxidising melting of the same in a reverberatory furnace. By this process (Ger. "*abtreiben, vertreiben,* or *treiben*") the lead is converted into oxide, which is withdrawn from the furnace in a molten condition, whilst the silver remains after all the lead has been oxidised.

The oxidation of the lead is effected by means of the oxygen of the air, this acting for the most part directly, though a portion of the lead may be oxidised by oxygen acting indirectly, litharge acting as the medium. Litharge possesses the property of absorbing oxygen from the air when melted in contact with it, and it gives up this oxygen to lead and other oxidisable metals.

During the cupellation the temperature must be maintained at such a point that the lead oxide is thoroughly fluid, and can flow from the furnace without mechanically enclosing any appreciable quantity of work-lead or silver.

The cupellation process can be conducted in three ways :—

(1.) In the first method the cupellation is only carried up to a certain point until the lead contains 50 to 80 per cent. of silver, this enriched alloy being then cupelled in a separate furnace.

(2.) In the second method the cupellation is carried further and an impure silver (*blicksilber*) containing about 10 per cent. of other metals, is obtained. When *blicksilber* is produced, it is submitted to further cupellation (*feinbrennen* or *raffiniren*) and converted into fine silver.

(3.) In this method the work-lead or the previously concentrated alloy is cupelled directly to pure silver (*feinsilber*).

The various impurities present in the lead behave during the cupellation in much the same way as in the refining or softening of lead in reverberatory furnaces. During the melting of the lead, mechanically mixed impurities, such as metallic sulphides and slag, separate completely, and most of the copper, cobalt and nickel also separate. The other metals and the remainder of the cobalt and nickel are converted into oxides by the action of the oxygen of the air on the bath, zinc, iron, tin, cobalt and nickel being the most easily oxidised. Arsenic and antimony require a much longer time for their oxidation, and bismuth is the most difficult of all the metals

to oxidise, so much so that it is only got rid of in the last portions of the litharge produced in the process, and a minute quantity often remains in the fine silver obtained.

As soon as the formation of litharge begins, as already mentioned, it acts as an oxidising agent, not merely owing to its power of dissolving oxygen, but by a chemical change, whereby its combined oxygen may be used to oxidise any copper present in the bath, the litharge being reduced to metallic lead. This oxidation of copper by litharge, in which the usual relations between lead and copper and oxygen are reversed, is ascribed to the action of mass, and, in fact, only a small proportion of copper can be oxidised by a large amount of litharge. If large quantities of copper are present, part of it remains behind with the silver, and lead rich in copper must therefore be liquated before cupellation if the silver is desired free from copper.

In the reverse way, lead is oxidised by cuprous oxide if the latter is present in large quantities (Berthier).

A loss of silver may arise owing to the fact that the litharge mechanically encloses small particles of argentiferous lead. In the first period of the cupellation this loss is so slight as to be scarcely noticeable, but it increases as the bath becomes richer in silver and reaches its highest point during the last stage of the process. To what extent silver itself is oxidised during the process and taken up by the litharge is a question which has not been satisfactorily answered. At all events argentiferous litharge can be deprived of its silver by prolonged contact with lead which is not too rich in silver; but whether this desilverising of the litharge is merely due to the little particles of argentiferous lead in it uniting with the rest of the lead (as when the residue from the extraction of the dross formed by treating zinc scums by steam in the zinc desilverising process, is added to the cupellation process), or whether it is due to a reduction of some silver oxide, has not been settled. Any gold present in the work-lead remains behind with the silver, only minute traces being found in the litharge.

There are two kinds of reverberatory furnace in which the process of cupellation is conducted—the German and the English furnace. The German furnace possesses a fixed hearth which forms part of the furnace and is capable of holding a large charge of lead, whilst the English furnace has a movable hearth of much smaller capacity than the German one. In the German the hood or portion covering the hearth is removable, whilst the roof of the English furnace forms an integral part of it. The method of working is also

different, as in the German furnace the various oxidised scums are withdrawn in separate portions (*abzug*, *abstrich* and *glätte*), and the lead is cupelled either with or without a previous concentrating cupellation, until *blicksilber* is produced, the process being rarely carried in one operation as far as fine silver. In the English process the various oxides are not separated from one another, and the work-lead is as a rule first submitted to a special concentrating cupellation and is then cupelled for fine silver. The production of *blicksilber*, which is the rule in German furnaces, is not carried out in English ones.

The German furnace is used chiefly when the object is to produce a marketable litharge, to obtain any bismuth present in the later portions of the litharge, and where large quantities of argentiferous ores and metallurgical products are to be added to the lead bath in the furnace.

The English furnace, which has of recent years been variously improved in American works, is used where very rich lead is to be cupelled, in which case the litharge is too rich in silver to allow of it being sold, and in such cases the improved English furnace is to be preferred to the German model.

In both processes, owing to the comparatively high temperature which is necessary in order to melt the litharge, a considerable amount of lead is volatilised, carrying with it a considerable amount of silver, and it is consequently necessary to provide the cupellation furnace with some arrangement for condensing this fume. Usually extensive flues are used with hanging partitions [1] or occasionally water condensers, and the working openings of the furnace are usually provided with hoods to protect the workmen from the fumes.

Cupellation in the German Furnace

The German furnace is a reverberatory furnace, with either circular, square or oval hearth. The material of which the latter is composed must be such that it neither exerts any reducing action upon the lead oxide nor is fluxed by it, and it must not crack at the temperature employed. Certain kinds of marl possess these properties, as does also a mixture of clay and limestone, composed of one measure of clay to 3 or 4 of limestone. Formerly, lixiviated and calcined wood ashes were used as the hearth material; but this material was not only more costly than marl, but, on account of its porosity, it absorbed a large amount of litharge and gave rise to considerable losses

[1] See the author's *General Metallurgy*.

of lead and silver when the broken-up hearth had to be smelted. For these reasons it is no longer used.

The natural marl used at the smelting works in the Harz is found in the chalk (*gault*) near Langelsheim, and is a mixture of calcium carbonate and clay, containing :—

65 to 66	per cent.	of Calcium carbonate
5 to 7	„	Alumina
21 to 24	„	Silica
3 to 5	„	Oxide of iron
1 to 2	„	Magnesium carbonate

Natural marls poor in lime receive an addition of limestone, whilst, if poor in clay, that material is added to them in the requisite quantity. If the marl contains too much clay it cracks readily, and if too much calcium carbonate is present, the hearth becomes too porous and is liable to lift on heating.

The marl is first stamped to powder and sieved, and is then mixed with such a quantity of water that it can be pressed into balls by the hand without actually feeling damp. It is stamped on to the floor of the hearth until it will not take the imprint of the finger, the exact degree of solidity being of great importance, a too compact hearth easily cracking, whilst a too porous one absorbs too much litharge.

The hearth is usually stamped down on a layer of fire-resisting material, resting in its turn on a bed of bricks or slag. This under layer is supported by masonry, below which is the furnace foundation. In this and in the other masonry of the furnace are cross channels for conducting away any moisture. The thickness of the marl hearth is about 8 inches, but it is made rather thicker at the edges, and at the working opening (*glättloch*). The litharge flows over the bottom of this opening, which is made from the material of the hearth with a channel cut in it through which the litharge flows. As the level of the molten metal is gradually reduced, this channel is deepened by scraping it out, in order that the litharge can still flow away. In order to prevent the litharge soaking through and finding its way to the brick or slag bottom, the marl hearth has at times been built up in an iron pan, but this iron dish is not in general use. After the hearth has been stamped down, a circular depression about three quarters of an inch deep is cut out (*blickspur*), the size depending upon the amount of *blicksilber* that is to be collected, with the object of facilitating the collecting of the latter.

The cover of the hearth is in the shape of a flat dome, and is so

arranged that it can be removed by means of a crane fixed to the side walls of the furnace. By the removal of this cover the cooling of the hearth is facilitated, and, as after each cupellation a fresh hearth must be made, the breaking up of the old one is more easily effected. Formerly the hearth cover was composed entirely of iron plate, having a clay lining held up by iron spirals fastened all over the iron cover, but at present it is constructed of a wrought-iron frame lined with firebrick. The furnace is heated either with bituminous coal, brown coal, wood or peat, gas firing having only been tried experimentally. If a coal fire is used the grate is generally closed, and a blast injected below it.

From one to three tuyeres are used for the admission of the blast over the surface of the bath, and these are usually provided at the nozzles with means of adjustment, by which the air can be directed so as to strike the bath at the proper angle. The tuyeres are so inclined to each other that the blast meets in the centre of the bath. They are placed somewhat obliquely opposite the litharge outlet, so that the outflowing litharge shall not be too rich in silver. The cupellation furnaces hold from 5 to 30 tons of work-lead.

As types of the various forms of this furnace, the older and newer ones at Lautenthal, and the large furnaces at Przibram and Freiberg are given below.

The old Lautenthal furnace is shown in Figs. 367 and 368; *r* is the grate with blast pipe *w* below, *m* is the hearth chamber, *f* the flue divided by fireclay partitions into several openings, and *n* the movable cover. The marl hearth *i*, rests upon a layer of firebrick, and the latter on the masonry, *z*, which is kept dry by two intersecting channels in it. The tuyeres are laid in the openings *x*, and the litharge formed on the surface of the bath by the action of this blast is drawn off through a channel cut in the bottom of the litharge outlet *g*. A hood to protect the worker from the fumes is placed over this outlet, and is connected by means of the sheet-iron pipe *p* to the flue. The charge for this furnace amounts to 10 tons of work-lead.

The newer furnace at Lautenthal is arranged as shown in Figs. 369 to 374, Figs. 375 and 376 showing the construction of the firebrick cover, the adjacent bricks being bound together by iron pins, *b*. The charge for this furnace is 10 or 11 tons of work-lead.

The large furnace of Przibram, designed by Czermak, is illustrated by Figs. 377 to 380. It was at first fired by gas, but was afterwards altered to burn coal. The hearth is square, with rounded corners; *b*, *b* are the grates with blast below them, air being conveyed by the pipes *k*. The flames from the grate pass along the channel *c* into the hearth

chamber, and the waste gases pass along the flues *d*, *d*, into the vertical passages *e*, *e*, *e*, and thence through the dust collectors, into the chimney. The firing can be regulated by the damper *f*. The marl

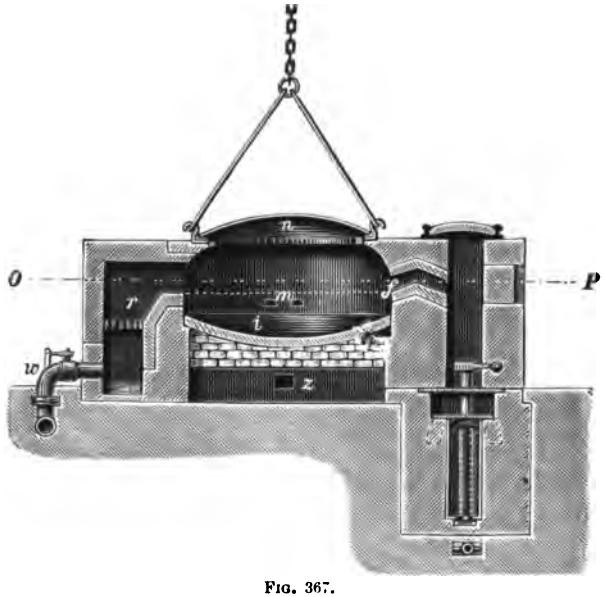


FIG. 367.

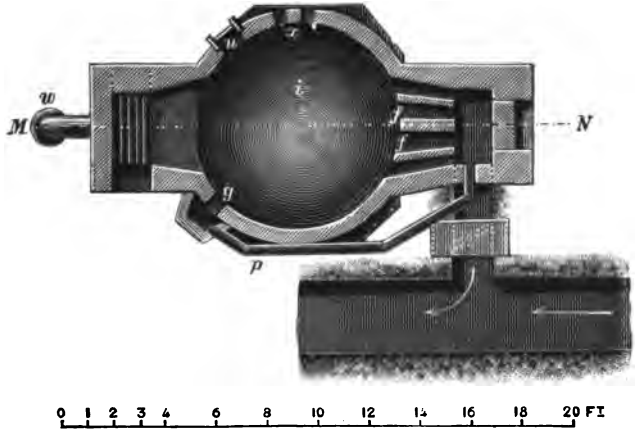


FIG. 368.

hearth, *n*, composed of 3 parts limestone and 1 of clay, rests on an under hearth of solidly stamped marl, the latter supported by masonry, having channels as shown in the figure to secure it against damp;

i is the cover, *a*, *a*, *a* are openings for the introduction of the three tuyeres, and *h* is the litharge outlet. This can be closed by a sliding door, *o*, in order to protect the workmen from the lead fume, and the

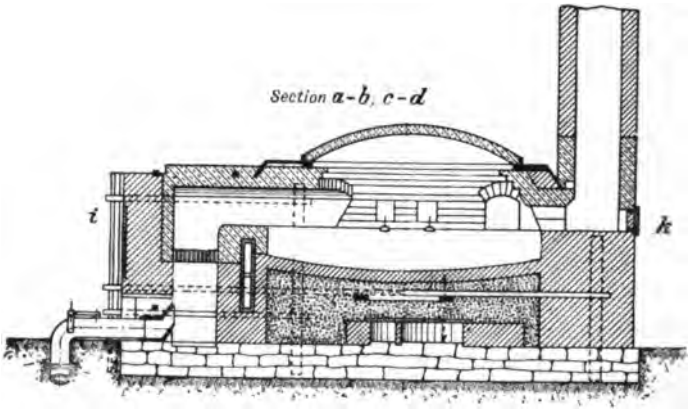


FIG. 369.

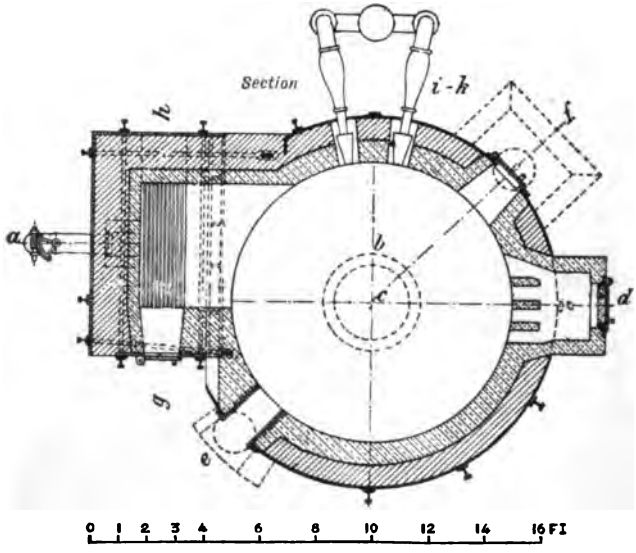


FIG. 370.

litharge is tapped periodically by removing a clay plug from the litharge outlet, and allowing it to run out. The circular depression, *g*, (*blickspur*) is for the collection of the silver (*blicksilber*) at the conclusion of the operation.

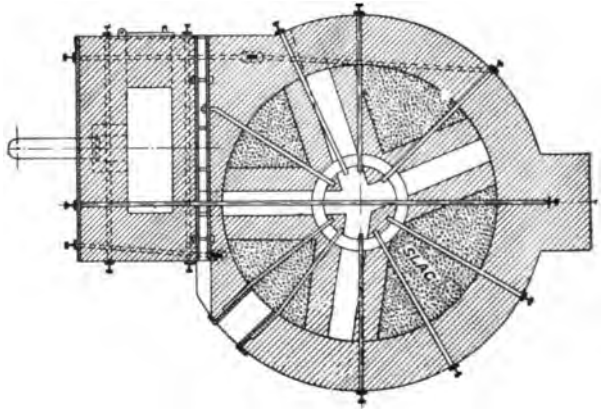


FIG. 371.

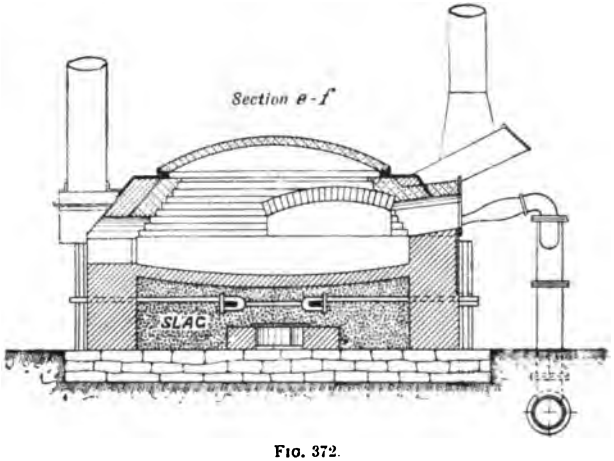


FIG. 372.

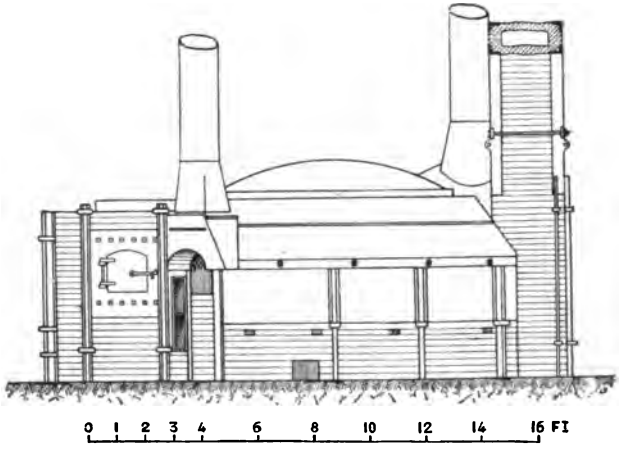


FIG. 373.

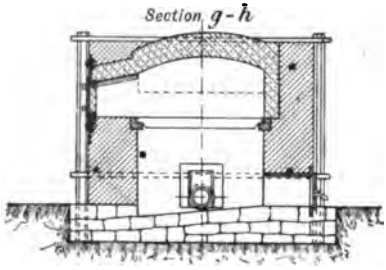
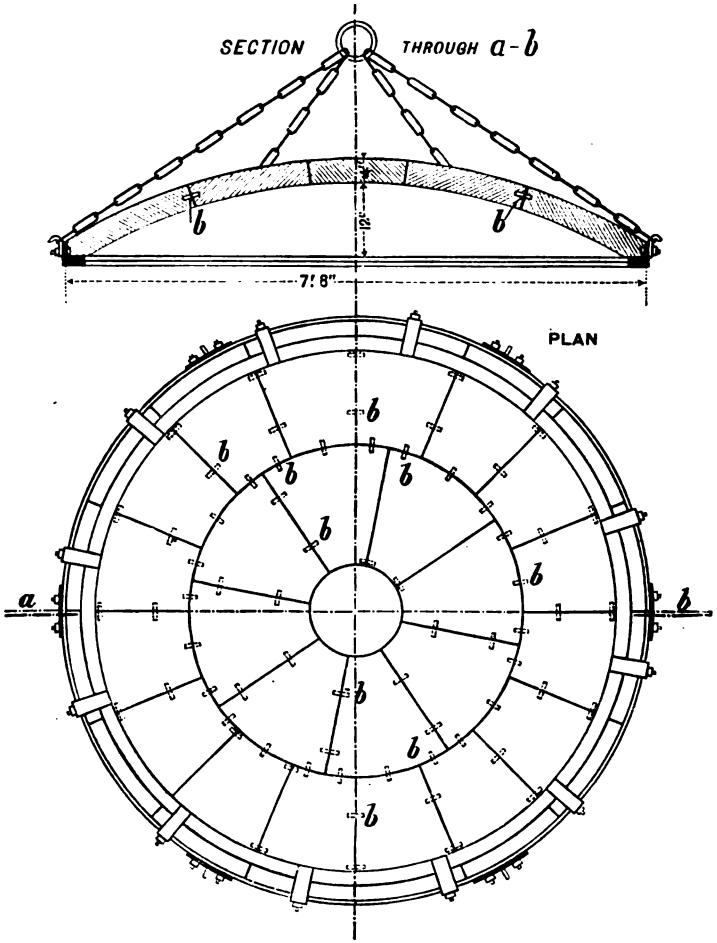


FIG. 374.



FIGS. 375 and 376.

The charge in this furnace amounts to 22·5 to 25 tons of work-lead and this large furnace is found to give better results than the smaller one at Przibram.

The large cupellation hearth, designed by Plattner and in use at Freiberg, is shown in Figs. 381 to 386. It is an oblong furnace with

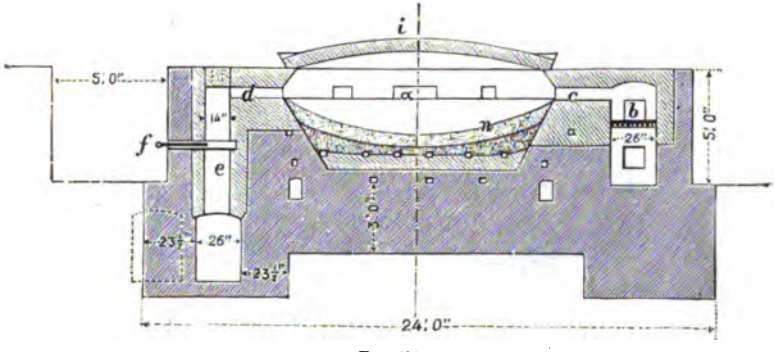


Fig. 377.

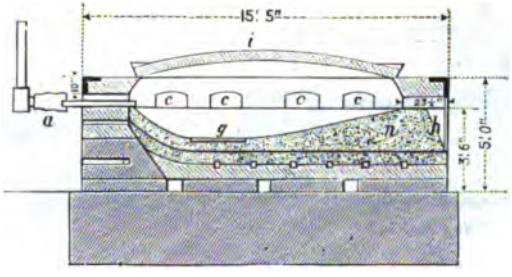


Fig. 378.

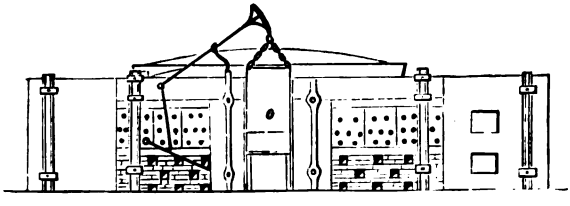


Fig. 379.

elliptical hearth, *a* being the firegrate, the air for combustion being introduced below by the pipe *c*; *w* is the firebridge, built hollow so as to allow of air cooling. The marl hearth, *z*, is composed of a mixture of three parts of Meissen clay and two parts Silesian marl. Below this is a layer of firebrick, and under this a bed of slag, *x*, resting on

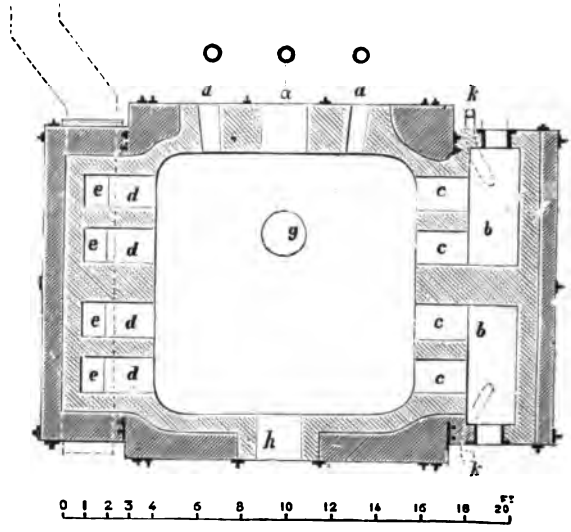
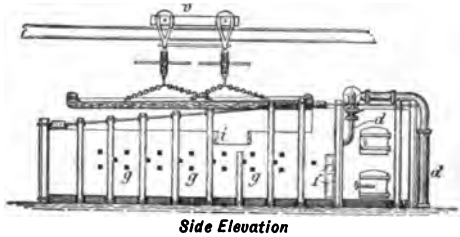
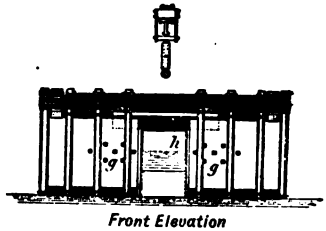


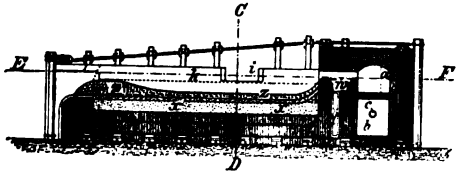
FIG. 380.



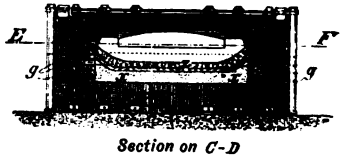
Side Elevation



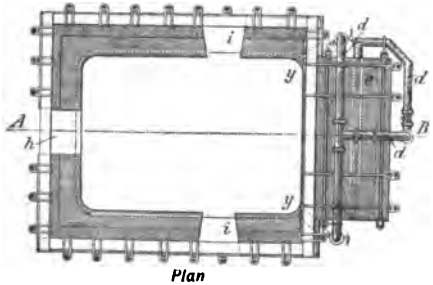
Front Elevation



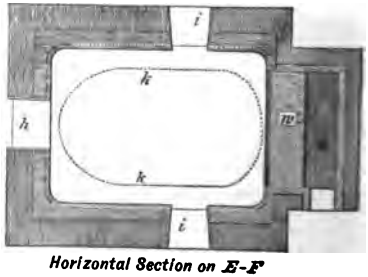
Section on A-B



Section on C-D



Plan



Horizontal Section on E-F

FIGS. 381—386.

masonry. The foundation plate, *e*, is of cast iron, and below this are channels to keep the foundations dry. The pipe, *d*, conveys the blast for oxidation to the tuyeres placed at the two corners of the furnace, *y*, *y*; *h* is the litharge outlet, *i*, *i* the doors for the introduction of the lead, and *v* is the crane for removing the hearth cover. The chief dimensions of the furnace are as follows:—length of hearth 13ft. 1½in., breadth 8ft. 8in., length of firebridge 6ft. 7in., breadth 29½in., height above grate 8in., height above lowest point of hearth 16in., length of grate 6ft. 7in., breadth 2ft., distance between the two tuyeres 8ft. 2in., distance between hearth and cover 31½in., breadth of litharge outlet 35½in., height of same above the hearth bottom 33½in. The waste gases pass through the litharge outlet, and pass along a flue into the dust chamber. This furnace is used for concentrating the rich lead up to a certain point (80 per cent. silver), and, owing to the great length of the hearth, it is difficult to maintain the requisite temperature towards the end of the process. From 50 to 60 tons of work-lead are enriched up to 80 per cent. of silver in a campaign of 7 to 10 days.

The Process

After the hearth has been stamped in, the charging of the furnace with work-lead begins. The amount of work-lead to be cupelled is either just sufficient to fill the hearth or else is more than sufficient; and in this latter case, after the cupellation has gone on for some time and the level of the bath sinks so that litharge no longer flows out, a quantity of lead equivalent to that which has been oxidised is again charged in. This is repeated, fresh additions of lead being made until the whole has been introduced. The added lead must be pure, otherwise the impurities which in the first charge were removed with the first scum, would collect in the litharge and render it unsaleable. If a marketable litharge is to be made, impure leads must therefore be refined beforehand.

After the charge is introduced, the hearth cover is placed in position and the melting down of the lead is begun.

The lead is melted very slowly, in order that any mechanically contained impurities may have an opportunity of separating. These impurities consist of metallic sulphides, and the greater part of the copper contained in the lead, as well as other easily oxidisable constituents, and separate as a dark coloured imperfectly fluid mass, which can easily be raked off the surface with a faggot of wood stuck on the end of an iron rod. This product, known as *abzug*, is only formed

when very impure lead is being worked, and is afterwards smelted, yielding work-lead and matte.

After the separation of the *abzug*, the blast is turned on, and any antimony and arsenic present are oxidised with the production of arseniate and antimoniate of lead, which, together with some litharge, form a viscid dark-coloured scum known as *abstrich*.

This *abstrich* is raked off as formed and afterwards smelted separately for hard lead. A high proportion of antimony, needing much time for its removal, greatly retards cupellation, as no litharge forms until the antimony has been got rid of. The later portions of the *abstrich* contain a large admixture of litharge; and after the *abstrich* has ceased to form, pure litharge (*glätte*) begins to be produced, and this continues until the end of the cupellation when the blicksilber is left.

As soon as the *abzug* has been separated, bubbles of gas are given off from the surface of the lead, and this appearance (*heerddrang*) continues during the whole litharge period. It is chiefly due to steam given off from the hearth, and in a less degree to carbon dioxide due to the action of heat and of lead oxide upon the calcium carbonate in the material of the hearth.

The molten litharge is drawn off through the channel formed at the bottom of the litharge outlet by means of a rabble (*glätthaken*), the action of the blast tending to carry it towards this outlet, the channel being deepened as the cupellation proceeds. In order to diminish the loss of lead by volatilisation the operation is so conducted that the bath of metal is kept covered with litharge for a space of from 12 to 19½ inches from its edge, and so that the litharge ceases to flow as soon as the blast is turned off. At some works the litharge is allowed to completely cover the bath of metal, and is only tapped periodically. The furnace temperature also must be carefully regulated so as to avoid loss by excessive volatilisation, though, as the lead becomes richer in silver and less fusible, and the space above it becomes greater, both the quantity and pressure of the blast must be increased.

The amount of blast in a circular furnace of 8 feet diameter, at the commencement of the process, is from 106 to 143 cubic feet per minute, and afterwards 211 to 282 cubic feet, whilst the pressure varies from ¾ to 1 inch of mercury.

The first-formed litharge possesses a dark green or brown colour, and is impure owing to the presence of various elements, but particularly of the last portions of the antimony and copper, and is known as "*foot*" litharge (*fussglätte*) or "*black*" or "*wild*" litharge (*schwarze*

glätte, wilde glätte). It is not marketable even when poor lead is being treated, and is smelted for work-lead.

The litharge which forms next, when rich lead such as that obtained by the zinc process is being cupelled, is rich in silver, and is consequently also smelted for work-lead, being either added to the ore or matte smelting process or worked up alone.

If the lead undergoing cupellation is poor, the litharge, with the exception of the latter portions, is also poor in silver, and is either sold as such, or is smelted for market lead either alone or with other lead bye-products poor in silver.

The litharge, whether poor or rich in silver, may have a yellow or red colour though presenting no differences whatever in chemical composition. The yellow form, known as *silver* litharge, is produced when molten litharge is quickly cooled, as when, for instance, it is allowed to flow from the furnace on to an iron plate and is then cooled by water.

The red or *gold* litharge is produced by slow cooling when, for instance, large masses of molten litharge slowly solidify, this being attained by allowing the litharge to flow into large receivers placed in front of the litharge outlet of the hearth. The masses obtained in this way break up on cooling, forming after a little time an easily disintegrated friable mass of small red scales or flakes. This disintegration is due to the absorption of oxygen from the air by the molten litharge, the gas being again given out on cooling.

The yellow litharge is "*freshened*," that is, reduced to metallic lead, whilst the red variety, if from the cupellation of poor lead, is broken up and sieved, and sent to market.

The latter portions of the litharge, even in the cupellation of lead poor in silver, are argentiferous and are therefore smelted for work-lead or else used as a *leading* material for silver ores or argentiferous smelting products.

In the cupellation of lead containing bismuth, the latter portions of the litharge are found to contain that metal, and they are "*freshened*" with the production of a lead rich in bismuth. On cupelling the latter, a litharge still richer in bismuth oxide is obtained, and this is worked up for the metal or its salts in the wet way.

Towards the end of the cupellation the last portions of the litharge collect together in the form of coloured rings (*glättaugen*) and this appearance, which precedes the *brightening*, is known as the "*flowering*" (*blumen*) of the silver. The appearance is due to the fact that the layer of litharge is not sufficient to completely cover the surface of the silver, and forms a sort of network over it, through

which the bright metallic surface can be seen. At the end of the operation this litharge finds its way to the edges of the bath, leaving the bright surface with a mirror-like appearance, and this last stage is called the *brightening* or *blicken* of the silver.

The *blicksilber* obtained in this way still contains from 5 to 10 per cent. of impurity consisting of lead, bismuth or copper. In most works after it has solidified, it is cooled with water, withdrawn from the furnace, broken into pieces and submitted afresh to the cupellation process in a different furnace, this refining operation being known as fine-burning (*feinbrennen*).

In some places the refining operation is conducted in the same furnace, necessitating the employment of a much higher temperature than in the previous cupellation.

In order to separate copper from the *blicksilber*, lead is added to it whilst in the furnace, and the process of cupellation is continued, the copper being oxidised and carried off with the litharge.

If the cupellation is not to be carried as far as the *brightening* stage, it is interrupted when the lead has been sufficiently enriched (up to 40 to 80 per cent. of silver). This enriched lead is then ladled or tapped out of the furnace and recupelled either for *blicksilber* or directly to fine silver. This enriching of the lead is called cupellation to "*schwarzblick*," the enriched alloy being called "*schwarzblick*" or "*bleileder*," and the method is principally used when the object is to obtain the bismuth contained in the lead, as at Freiberg.

In this method of enriching, a part of the lead is subsequently charged; these additions begin when litharge commences to form.

The top portions of the marl hearth absorb considerable amounts of litharge, and where bismuth is present it collects chiefly in those portions lying nearest the *blicksilber*. The portions of the hearth saturated with litharge are broken up after each cupellation, and either used as a *leading* material in the smelting of silver ores, or else they are smelted alone for work-lead. The portions rich in bismuth are worked up in the same way as the litharge which contains bismuth. The hearth is broken up after the furnace has cooled down, and after the grains and pieces of silver embedded in the hearth have been picked out. The portions of the hearth free from litharge are used again in the preparation of the next hearth.

There is a considerable loss of lead in cupellation and a smaller loss of silver. The lead loss is either direct or indirect, the direct loss being partly caused by volatilisation owing to the comparatively high temperature, and partly by the fact that the litharge carries away particles of lead. The indirect loss is that which takes place

during the smelting of the litharge and the litharge-soaked hearth, when part of the lead is lost in the slag. The volatilisation loss increases with the temperature, whilst if the cupellation be conducted more slowly and at a lower temperature, the loss owing to particles of lead being carried away by the litharge becomes greater. The total loss of lead varies from 3 to 8 per cent. of the weight of the lead cupelled.

The loss of silver is partly due to volatilisation and partly to losses in the smelting of the litharge and hearth, whereby a portion of the silver goes into the slag. The total silver loss is less than 1 per cent. and usually below 0·5 per cent.

The time taken in the cupellation process varies according to the weight of the charge and the character and amount of the impurities contained in it from 20 to 300 hours, the presence of antimony in particular much prolonging the process.

The coal consumption amounts to from 20 to 30 per cent. of the weight of the lead, varying with the purity of the lead and the type of furnace used.

The products of the operation are—*Blicksilber* or fine silver, *scums* (*abzug*, *abstrich*), litharge and *hearth* (that is, litharge-saturated hearth).

The *blicksilber* contains from 5 to 10 per cent. of foreign metals, the composition of three samples being given below:—

	Przibram.	Freiberg.	Wyandotte (Michigan).
Silver	95	92·18	98·691
Lead	5	4·21	1·09
Copper	—	2·104	0·117
Nickel and Cobalt	—	0·6	0·004
Iron	—	—	0·09
Bismuth	—	—	0·0058
Gold	—	—	0·0023

The *abzug* varies in composition chiefly as regards the copper and metallic sulphides it contains. *Abzug* from Pontgibaud had the following composition:—

	Sample 1.	Sample 2.
Lead monoxide	37·9	56·2
Cupric oxide	5·0	1·2
Ferric oxide	5·8	5·7
Zinc oxide	5·4	4·9
Antimony oxide	5·2	0·5
Sulphur	7·3	—
Lead	34·9	24·4

Samples of *abstrich* from three localities gave the following results on analysis :—

	Freiberg.	Altenau.	Kapnik (Hungary).
Lead monoxide	95·5	67·13	53·28
Cupric oxide	0·5	traces	0·05
Ferric oxide	0·3		0·58
Zinc oxide	1·1	0·38	—
Antimony oxide (Sb_2O_3)	—	31·1	42·9
Arsenious oxide	2·3	—	2·34
Sulphur	—	2·23	0·07
Lead	—	—	0·45

The composition of three samples of litharge (*bleiglätte*) is given below :—

	Freiberg.	Clausthal.	Przibram.
Lead monoxide	96·21	99·69	97·88
Cupric oxide	0·82	0·04	0·24
Ferric oxide	0·41	traces	traces
Zinc oxide	1·31	—	—
Silver oxide	0·003	—	0·002
Antimonic and Arsenic oxides.	1·21	—	traces
Lime	—	—	0·24
Alumina	—	—	0·07
Carbon dioxide	—	—	0·1
Silica	—	—	0·66

The amount of silver in the litharge is dependent upon the amount in the work-lead, and with rich varieties it is seldom less than 0·02 or 0·03 per cent.

The composition of a sample of the litharge-soaked hearth from the Przibram furnaces was found to be as follows :—

Lead monoxide	68·86	Ferric oxide	0·3
Cupric oxide	0·07	Calcium carbonate	24·1
Antimony oxide (Sb_2O_5)	0·53	Silica	2·97
Silver oxide	0·17	Sulphuric anhydride	0·04
Alumina	2·12		

Here again the amount of silver present depends upon the richness of the cupelled lead, varying in the Upper Harz from 0·03 to 0·2 per cent.

The cupellation process is conducted either by (*a*) placing the entire quantity of work-lead in the furnace at the beginning of the operation (*treiben ohne Nachsetzen*) or else (*b*) only a portion of the lead

is put in and the rest added at intervals as the lead becomes oxidised (*mit Nachsetzen*); details of both these processes will be found below.

(*a*) Cupellation without Additions of Lead (*ohne Nachsetzen*)

At the Rothenbach works near Müsen, in the Siegen district, 25½ tons of work-lead rich in antimony are placed in a furnace, the hearth of which is 10 feet 3 inches in diameter, and this is cupelled for *blicksilber* in 300 hours. Of this period 3 hours are occupied in charging, 24 to 27 hours in melting, the *abzug* period lasts 9 hours, the *abstrich* formation goes on for 144 hours, and the production of litharge for 117 hours. The fuel used is wood, of which 21 cubic feet are used for every 5 tons of work-lead. From every 100 parts of work-lead 7·6 parts of *abzug*, 21 parts of *abstrich*, 52 parts of impure litharge, 30 parts of "silver" and "gold" litharge containing 0·004 to 0·006 per cent. of silver, and 0·28 parts of *blicksilber* are produced. The "silver" and "gold" litharge are sent to market.

At the Lautenthal works 6 tons of rich work-lead from the zinc desilverising process are charged into the furnace previously described (page 570). After the litharge period commences, a mixture of lead oxide and shots of lead is added to the bath (*eingetränkt*), and the whole process, including this operation, lasts 32 hours. For each operation 14 to 15 cwt. of coal are used, and 12 to 15 score bundles of faggots. One workman and one fireman are required for each shift.

At the Clausthal works impure work-lead from matte smelting with the following average composition is cupelled :—

Bismuth .	0·00301 per cent.	Zinc	0·0012 per cent.
Copper .	0·502 „	Nickel. . . .	0·00504 „
Antimony .	0·8278 „	Silver	0·353 „
Iron . . .	0·0018 „	Lead	98·30615 „

The hearth is 8 feet 3 inches in diameter, and the charge of 10 tons of work-lead requires 36 hours to work off. Of this time 2 hours are used for forming the hearth and charging, 2 hours for melting and drawing off the *abzug*, the *abstrich* period lasting 4 hours, and the litharge period 28 hours. Each cupellation requires on an average 200 bundles of wood (faggots) and 1·3 to 1·4 tons of coal, and from 10 tons of work-lead the yields are 37 lbs. of *blicksilber*, 8·6 tons of litharge, containing 0·005 per cent. of silver, ½ ton of *abzug* and *abstrich*, and about 1·8 tons of hearth, impregnated with

litharge. During each 12-hourly shift the services of one workman and one fireman are required.

At Altenau and also at Andreasberg, additions of argentiferous metallurgical products and rich silver ores are made during the cupellation. The duration of the operation with 10 to 12 tons of work-lead varies according to the amount of the materials added from 24 to 36 hours, and the amounts of the various products from both works, taken over a long working period, are as follows :—

ALTENAU

Charge . . .	1749·2 tons	work-lead.
Materials added : (*eingetränkt*)	2·5 „	silver slimes (from the electrolytic process and sulphuric acid extraction).
„	5·604 „	foreign ores.
„	10·05 „	*abzug* from a former operation.
„	9·2 „	rich oxide (from the treatment of the rich scums with steam).
Fuel consumption .	189 tons	coal.
„ „	8103 faggots	of wood.
Hearth material .	4633 cubic feet	of marl.
„ „	850 cubic feet	of clay slate.

ANDREASBERG

Charge	2312·4 tons	work-lead.
Materials added : (*eingetränkt*)	7·3 „	tons of ore.
„	1·21 „	slag from fine cupellation.
„	1·6 „	rich oxides (from the treatment of rich scum with steam).
	6·38 „	metallurgical bye-products.
Fuel consumption . .	317·1 „	of coal.
„ „	485	cubic yards of wood.
Hearth material . .	212 tons	of marl.
„ „	3,000	cubic feet of clay slate.

The labour required is the same as for the Lautenthal and Clausthal furnaces.

At Hoboken, near Antwerp, the cupellation furnace is similar to the later form of Lautenthal furnace, which has already been described, and the charge consists of 10 tons of work-lead. To this is added from 60 to 100 per cent. of its weight of argentiferous products (residues

from the rich scum distillation, lixiviated oxides from the treatment of the rich scum with steam, and silver slimes from the treatment of the zinc-silver alloy with sulphuric acid). The cupellation lasts from 36 to 40 hours, and the coal consumption amounts to 20 to 25 per cent. of the total weight of the materials treated, one workman and one fireman being employed for each shift.

At Przibram, in Bohemia, 25 tons of work-lead, containing on an average 0·52 per cent. of silver, are cupelled in 80 hours in the large furnace described on p. 570.

The making of the hearth and the charging of the material occupies 8 hours, the melting 16 hours, the *abzug* period lasts 6 hours, the *abstrich* period 9 hours, and the litharge production goes on for 41 hours, during 23 hours of which marketable litharge, poor in silver, is being produced, the remaining 18 hours being the period of production of litharge rich in silver. The coal consumption amounts to 19·63 per cent. of the weight of the work-lead. Of the entire quantity of litharge, 36 per cent. is so poor in silver (0·004 per cent.) that it is sold as market litharge. The silver loss amounts to 0·83 per cent., and the loss of lead to 4·33 per cent., the losses arising during the working up of the products not being included. The furnace is worked on eight-hour shifts, with one workman and an assistant.

(*b*) Cupellation with Additions of Lead during the Process (*mit Nachsetzen*)

This process, the object of which is the production of enriched lead by a concentrating cupellation, is worked at Freiberg and Schemnitz.

In the older circular form of furnace at Freiberg, 10 tons of lead constitute the first charge, and 25 tons are added during the cupellation, and cupelled up to 70 or 80 per cent. of silver. The whole operation lasts from 100 to 102 hours, the blast pressure being 0·6 inch of mercury, and the fuel consumption 35·3 cubic feet of wood and 280 to 315 cubic feet of brown coal.

The enriched lead (*schwarzblick* or *bleileder*) is ladled from the hearth into cast-iron moulds, and then refined in a smaller hearth, yielding fine silver (998 fine) and bismuth litharge, 0·9 to 1·2 tons being worked at a time. The litharge with 4 to 8 per cent. of bismuth, and the hearth with 6 per cent. of bismuth, are treated in the wet way for that metal or its salts.

In the Plattner oval furnace described on p. 575, the amount of lead worked in each cupellation, including the additions, amounts to 50

to 60 tons, this being enriched up to 80 per cent. of silver, 50·85 tons requiring 178 hours for cupellation.[1] Every 100 parts of work-lead require 26·79 of brown coal, and 7·5 parts of marl for the hearth, and the products per 100 parts of work-lead are 12·52 parts of red marketable litharge, 75·59 parts of argentiferous litharge, and 11·75 parts of litharge-soaked hearth. The enriched lead is worked up in a smaller cupellation hearth to fine silver, and litharge rich in bismuth.

At Schemnitz, in Hungary, work-lead is similarly cupelled up to 50 per cent. of silver, the *schwarzblick* thus produced being further worked for *blicksilber*, and afterwards cupelled for fine silver. The Schemnitz cupellation furnace has a hearth 13 feet 1½ inches diameter, and holds 7 to 8 tons of lead, the amount of lead added during the process amounting to 20 to 30 tons, the cupellation lasting from 8 to 10 days. The litharge flows directly from the litharge outlet into an iron box filled with glowing charcoal, the so-called Siberian or Bernaul furnace, and is here reduced, the molten lead flowing away from the lower part; 4 cwts. of lead are reduced by 3·5 cubic feet (39 to 44 lbs.) of charcoal. The reduced lead contains antimony, from which it is freed by fusion in iron pots and treatment with steam; it is then treated with zinc in order to separate any silver and copper, and lastly, treated again with steam to get rid of the zinc. This purified lead is partly sent to market, and partly converted into "gold" litharge by cupellation. The fineness of the silver obtained varies from 990 to 997, and on an average 1 part of silver is obtained from 200 of work-lead. The average amount of gold present in the fine silver amounts to 25 parts per thousand. For every 10 tons of work-lead cupelled, 565 cubic feet of wood are required as fuel.

Cupellation in the English Furnace

The English furnace possesses a movable hearth but a fixed roof, and holds a much smaller amount of lead than the German furnace. The work in this furnace is generally so conducted that the work-lead with constant additions of lead is enriched up to a certain point, and then run out of the furnace: when a sufficient quantity has accumulated it is worked up for fine silver. The fine silver is rarely obtained from the work-lead in one operation.

The furnace hearth is built up in a movable frame called a *test ring*, the cupel itself being known as the *test*. Formerly bone ash was exclusively employed as the material for the test, but at present marl of similar composition to that used for the German furnace is also used, or cement, or a mixture of cement and fireclay.

[1] *Freiberger Jahrbuch*, 1885.

The movable hearth allows of the English furnace being worked continuously, because a hearth which needs repairing can be replaced by one previously prepared, time and fuel being in this way saved, whilst the capacity of the furnace is increased.

In the United States various improvements have been made in late years, with the result that the capacity of the furnaces has been enlarged, and the durability of the hearths has also been increased by

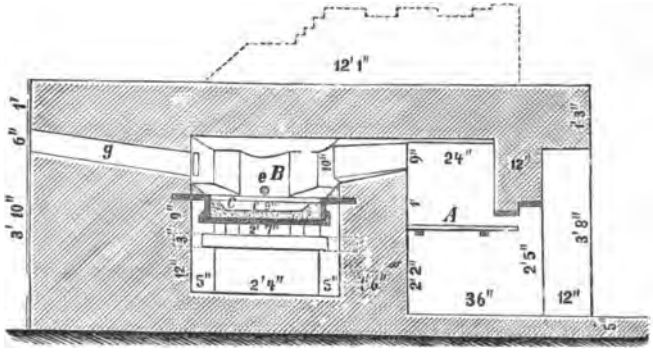


FIG. 387.

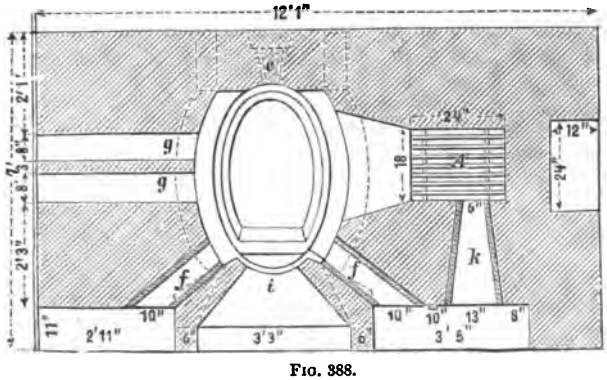


FIG. 388.

a more careful selection of materials and by the introduction of water cooling.

The English furnace in its later forms is preferable to the German hearth when rich silver-lead is to be cupelled and the litharge produced is too rich in silver to be sent to market.

The arrangement of the older form of English furnace is shown in Figs. 387 to 390. *A* is the grate, *B* the heating space, *c* the oval hearth, and *g* the flue, divided into two channels. The iron ring into which the bone ash or marl is rammed (Figs. 389 and 390) consists

of an elliptical wrought iron band *a*, with cross pieces *b*, the latter supporting the hearth. This test ring is first filled full of the compressed hearth material, and then the hollow cavity *c* is cut out of this. At one end channels *d*, *d*, *d* for the litharge are cut, the

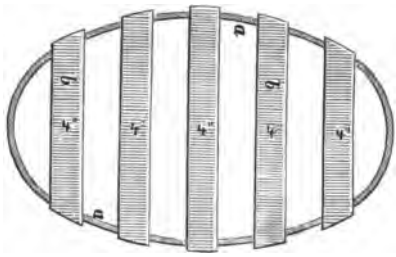


FIG. 389.

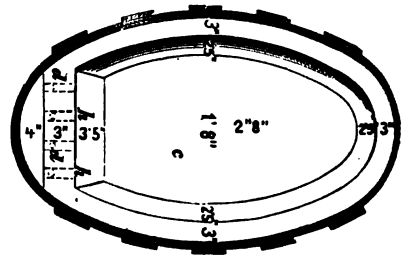
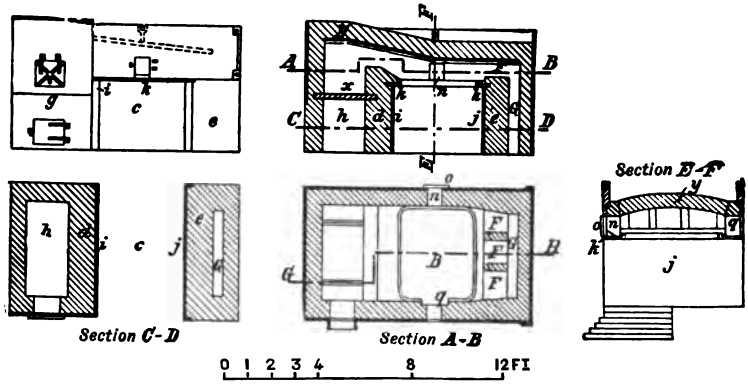


FIG. 390.

molten litharge flowing along these and then through a hole in the test into a receiver below the hearth. The test is encircled by a compass ring in the furnace and fixed firmly in position by four iron wedges, the joint between the test and the compass ring being filled in with some of the hearth material. The lead to be cupelled is either melted in a special cast iron pot and run from this into the hearth, or else it is placed in the passages *f*, *f*, where it melts and flows into the hearth; *i* is the working opening, and *e* is the opening for the tuyere supplying the air-blast for oxidation. The enriched lead



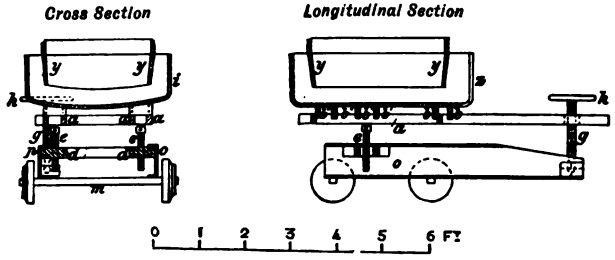
FIGS. 391—395.

is either ladled out of the cavity of the test or else tapped by boring a hole through the test bottom.

An American furnace[1] with rectangular hearth is shown in Figs. 391 to 395, where *x* is the grate, *B* the heating chamber, *F* the flue

[1] Hofman, *op. cit.*

divided into three channels by brick partitions for the purpose of spreading the flame equally over the surface of the bath. The waste gases pass away by the vertical flue G to the dust chambers, and the whole furnace is bound together with cast iron plates. The grate surface measures 4 feet 6 inches by 2 feet 9 inches, the hearth 4 feet 4 inches by 3 feet 6 inches; the roof y slopes sharply from the grate to the flue, so as to throw the heat on to the hearth; k is the compass ring, in which the test ring, supported on wheels, and not shown in the drawing, is placed. This ring is rectangular in shape with rounded corners, the ring being cut away at the litharge outlet q. The distance from the grate bars to the roof is 28 inches, and from



Figs. 396 and 397.

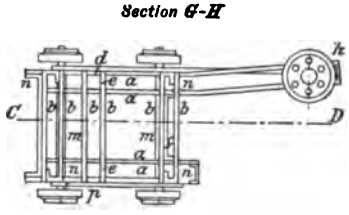


Fig. 398.

the roof to the upper edge of the compass ring $9\frac{1}{2}$ inches. At the far side of the furnace is an opening n, which can be closed by a sliding door o, and serves both for the introduction of the blast tuyere and for charging in the lead in pigs.

The test is shown in Figs. 396, 397 and 398. It is supported on wheels, and, like the compass ring into which it fits, is rectangular with round corners, this shape affording a greater surface for oxidation than the oval form. The iron mould y is only used in the building up of the hearth, the hearth material being rammed in all round it. The upper surface of the test lies on a level with the upper edge of the compass ring, and at the front the test has a slit z, 3 inches wide, serving as an outlet for the litharge, the slit being

closed whilst the hearth is being rammed into shape. The test can be raised or lowered by screws, as shown in the figure, the hindermost screws *e* raising the back portions of the frame *a*, whilst the screw *g* and handwheel *h* permit of its being raised or lowered from the front. The manipulation of the two back screws *e* during the working of the furnace being difficult, these screws are chiefly used to facilitate the introduction of the hearth into the compass ring and to support it during the operation.

Figs. 399 to 401 show a test with four supporting screws, by the aid of which it can be firmly fixed in the compass ring. As the

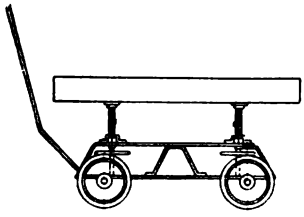


FIG. 399

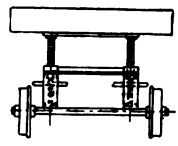


FIG. 400.

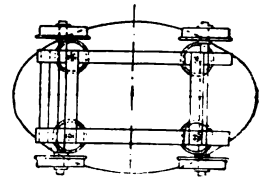


FIG. 401.

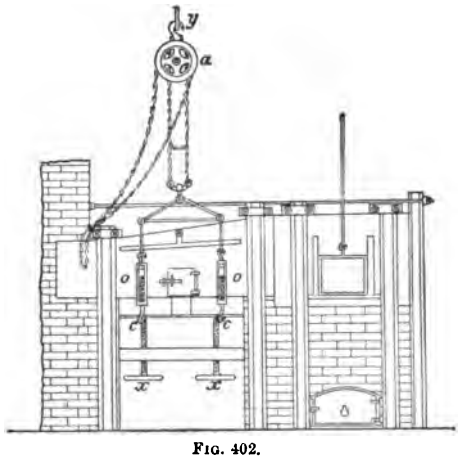


FIG. 402.

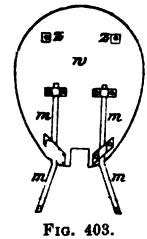


FIG. 403.

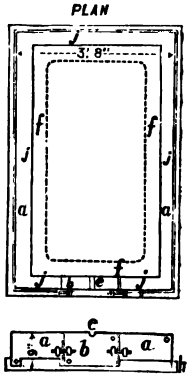
adjustment of these screws is difficult when the furnace is hot, the two front screws may be omitted and the test suspended at its front end. Such an arrangement, designed by Lynch,[1] is shown in Figs. 402 and 403, where the back portion of the test can be raised or lowered by screws *x*, *x*, the ends of which work in the holes *z*, *z*. At the front of the test, two iron bars *m*, *m* are fastened, and their projecting ends hook on to *o*, *o*, and by means of the differential pulley block *a*, the test can be readily raised or lowered. This can be

[1] Blake, *Trans. A.I.M.E.*, x., p. 220.

effected so very steadily and gently, that the flow of litharge can readily be regulated thereby, or the whole contents of the hearth, consisting of enriched lead or of silver, can be poured out.

Rösing[1] has suggested a movable hearth, which can be tipped by means of a toothed wheel, gearing in a toothed segment, fastened below the hearth, but this arrangement has not come into use. The movable form of hearth is generally adopted when the hearth is not completely cooled by water, and the flow of litharge is regulated by deepening the litharge channel, and is not used with water-cooled hearths with a fixed litharge channel incapable of being cut down.

In addition to the methods of fixing the test just mentioned, it may be firmly fastened in place by means of wedges. The hearths of some modern furnaces are kept cool by means of a water jacket in order to diminish the corrosive action of the litharge upon the material composing them. Either the breast of the hearth may be cooled in this way, or both the longer sides, or the entire hearth. When the breast is cooled, the iron composing the water jacket is protected from the action of the litharge by a coating of the hearth material 4 inches thick, the litharge channel in this case being cut out of the hearth itself.



Figs. 404 and 405.

The best method of applying water-cooling is by Steitz's system, where the entire sides of the hearth are jacketed, this arrangement being shown in Figs. 404 and 405; *j* is the rectangular jacket made of iron plate, and having on the front side a space in which a small cast iron water jacket *b* is placed. This smaller jacket is bolted on to the main one and has a channel *e* in its upper surface which acts as the litharge outlet. The hearth lining *f*, 4 inches thick, separates the fluid litharge from the jacket, and, like the latter, rests on the cast iron hearth plate *h*. The litharge outlet, however, being in direct contact with the fluid litharge, is soon attacked and eaten away, but owing to its construction it can easily be removed and replaced by a fresh one without interrupting the work.

This water-jacketed Steitz hearth is particularly suitable for the concentration of argentiferous lead, as in this operation the surface of the bath of molten metal can always be kept at a particular height; it is not, however, so well adapted to the cupellation for fine silver, owing to the level of the litharge outlet being fixed.

[1] *Berg. und Hüttenm. Ztg.*, 1883, p. 577.

The air necessary for oxidation was formerly obtained by a steam jet, but in the United States it is now usually furnished by some form of blower (Root's, Baker's or Sturtevant's), which delivers its air through a nozzle 3 inches in diameter. Some furnaces possess tuyeres whose nozzles are 4 inches long and ½ an inch wide. The pressure of the blast varies from 0·47 to 0·51 inch of mercury.

The hearths are only rarely now made of bone ash, but of a mixture of fire-clay and limestone, three parts of the latter being used to 2 or 3 of the former, or else of Portland cement, or of a mixture of 2 parts of Portland cement and 1 part of crushed firebrick. Hearths of magnesia bricks are also being tried experimentally. The material for the hearth is first moistened, as in the German process, and then rammed into the test frame, in many works the hearths being built up in three layers, in others the whole amount being rammed at once. The cavity in the marl hearths is cut out after the hearth has been rammed into position. The hearth border is 3 to 4 inches deep at the back and the two longer sides, and from 6 to 10 inches at the front, the thickness of the hearth being not less than 4 inches at the deepest point. This deepest point is placed near to the front of the hearth in order to render the tapping easier. The hollow in the hearth is about 5 inches deep. A hearth 4 feet 4 inches long, 2 feet 1 inch broad, and 5 inches deep holds 2¼ tons of work-lead, but recently hearths holding 5 tons (Omaha) and 6 tons (Balbach works near Newark) have been constructed.

If the hearth is composed of cement or of a mixture of cement and fireclay, the hollow must be constructed at the time of ramming the hearth.

In the case of tests having a continuous iron plate for the bottom, a layer of firebrick is usually put on the bottom, dried and then washed over with fire-clay. The sides are built up (Figs. 396 and 397) from the hearth material by ramming it between an iron mould and the side of the test frame.

After the hearth has been rammed into shape, it is dried for a fortnight in a warm place, usually adjoining the cupellation furnace. If it is put into the furnace when the latter is cold, it must be heated by a small charcoal fire, and if it is necessary to change the hearth whilst the furnace is at work, the new one must be very gently fired at first.

The operation is distinguished from that conducted in the German furnace in that the *abzug*, *abstrich* and litharge are not collected separately, and that the cupellation to fine silver is preceded by a cupellation which enriches the lead up to a certain point. In all

furnaces except the Steitz water-jacketed one, the litharge flows out through channels cut in the substance of the hearth, which gutters can be deepened as the operation proceeds. In order to avoid as far as possible the effects of the corrosion of the hearth by the litharge, several litharge outlets, usually 3 or 4, are made, and used one after the other. If a movable hearth be used, then the flow of the litharge can be readily regulated by raising or lowering the front of the test, and usually the rate of flow is so adjusted that about half of the surface of the molten metal is kept covered with litharge, the object being to avoid as far as possible excessive volatilisation of the lead.

In the Steitz furnace the flow of litharge is regulated only by the quantities of lead charged in; the litharge can be drawn off at intervals through the channel in the cast iron jacket, the channel being closed by a clay plug when not in use.

The outflowing litharge is received in movable cast iron pots placed below the litharge outlet, and, as it flows out, rich lead is added to the bath in order to maintain it at the same level. The additions of lead are made by placing a pig or two of lead in the opening at the far side of the furnace, and pushing them further into the furnace as they melt away.

The first cupellation is usually so conducted that the work-lead is enriched up to 60 or 70 per cent. of silver, the enriched silver-lead being ladled out of the furnace, and the hearth immediately receiving a fresh charge. After a time the hearth bottom gets so thin that it must be replaced by a fresh one, and the old one being drawn out, a new one is put in, and the working goes on with little interruption. Steitz's form of furnace is best suited for the concentration, because, with its fixed litharge outlet, it needs only unskilled labour to attend to it.

The duration of the hearth lining depends upon the material of which it is composed, upon the construction of the furnace, and the method of working. Thus, hearths of artificial marl used for concentration in a water-jacketed furnace last 60 days. At Port Pirie a furnace not water-jacketed, provided with a cement hearth holding ¾ of a ton of work-lead, concentrates 30 to 50 tons of work-lead from 15 per cent. up to 50 per cent. of silver.

The cupellation of the enriched silver-lead, in order to obtain fine silver, is usually done in an English form of hearth without water jacket. The operation is carried on in the same manner as the concentration cupellation, additions of work-lead being made until the hearth is nearly full of *blicksilber*, the temperature being gradually increased as the alloy becomes richer in silver. The *blicksilber* is

freed from the impurities it contains by the oxidising action of the blast, the oxidised impurities being collected by scattering a little marl or bone ash over the molten mass and then raking it off. Saltpetre is sometimes used to assist in the oxidation, and in the United States the silver obtained is at least 997 fine, its purity being ascertained by assay.

The fine silver is ladled out of the furnace into warm moulds, or where the Lynch furnace is used, it can be poured directly into the moulds. The cupellation for fine silver is not as a rule carried on continuously. Artificial marl hearths (clay and limestone), which are used daily for 4 or 5 hours, last about 30 days, a cement hearth lasting for months. If the cement hearth be used for both concentrating and refining, it only lasts seven days.

The bye-products obtained in the English process (scums, litharge, hearth and flue dust) are so rich in silver that they are smelted either alone or with other argentiferous materials for work-lead which is either cupelled directly or first enriched by the zinc process. The litharge contains at least 0·155 per cent. of silver, the amount easily reaching 0·622 per cent. when it is at all mixed with the scums from the work-lead. The loss of lead in the English furnace amounts to about 5 per cent.

In the United States,[1] in a hearth of the form previously described, 4 feet 6 inches long, and 3 feet 6 inches broad, 3·5 tons of rich lead with 10 per cent. of silver are enriched up to 70 per cent. of silver in 24 hours, 1½ to 2 tons of coal being used according to its quality, and one man's labour is required in each shift.

The cupellation of half a ton of this concentrated 70 per cent. alloy up to fine silver in a hearth 2 feet 9 inches long, 2 feet 4 inches broad, and 5 inches deep, requires 5 hours, 1½ tons of coal being burnt, and the services of one attendant being required.

At Port Pirie, South Australia, a cupellation furnace with water-cooled cement hearth, elliptical in shape, is used, its construction being shown in Figs. 406 to 410.

The charge for this furnace is 12 cwt., and in 8 hours 1 ton of work-lead can be enriched from 15 up to 50 per cent. of silver. This enriched alloy is then submitted to fine cupellation in a similar furnace in charges of 12 cwt., which require 8 hours to work off. The coal consumption amounts to 65 per cent. of the weight of the charge, and one man's labour is required. Each hearth can produce 5 to 6 tons of fine silver before it is necessary to renew it.

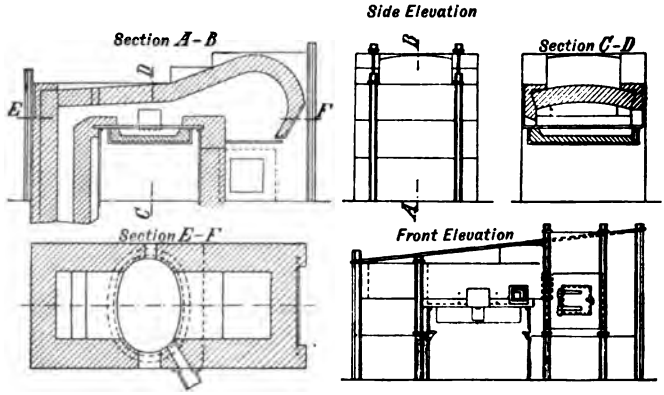
At Omaha (Nebraska) the artificial marl hearth holds 5 tons of

[1] Hofman, *The Metallurgy of Lead.*

lead, and the air is obtained by means of a steam jet. Three tons of coal are required for the cupellation of 5 tons of work-lead to *blicksilber*, and the marl hearth will work off 50 such charges.

The advantages possessed by the English form of furnace over the German one are—continuous working, and, as a result of this, a much greater output from the furnace, in proportion to its size—a smaller consumption of hearth material owing to the greater durability of the hearths, and consequently a smaller cost for labour connected with the hearth, and the production of less litharge-soaked and argentiferous hearth material. The indirect loss in the reduction of this hearth material is consequently smaller on account of its smaller quantity.

As regards fuel, the English furnace requires more than the large German furnace, but the cost for labour with the latter is greater, if



FIGS. 406—410.

the work connected with the hearth, mixing the materials, ramming them, breaking up the old hearth and smelting it, be taken into account. The German furnace also requires the labour of two workmen, the English furnace of only one.

The disadvantages of the English furnace are that litharge poor in silver or market litharge is not produced, and that there is a greater consumption of fuel. The English furnace is chiefly employed when the lead to be cupelled is so rich in silver that litharge poor in silver cannot be produced from it, this being usually the case where the zinc desilverising process is in use. The German form of furnace is chiefly used when the object is to obtain marketable litharge, which can only be done when the lead is poor in silver, or else when considerable amounts of silver ores or bye-products are to be added ("*eingetränkt*") to the bath of metal on the hearth.

The Refining of *Blicksilber*

The *blicksilber* obtained in the cupellation process still contains various impurities, such as copper, lead, bismuth, and more rarely nickel, antimony and arsenic. These can be almost entirely removed by melting and oxidising the molten metal with air, saltpetre or silver sulphate. Copper is the most difficult metal to remove, and where large quantities are present it is advisable to melt the metal with more lead and recupel it before refining. Bismuth is best got rid of by treatment with silver sulphate.

This purification of the *blicksilber* is known as refining or "fine-burning" (*feinbrennen*), and is either carried out in the ordinary cupellation hearth, or in a special refining hearth, in muffles, or in crucibles, the latter method being used when the silver sulphate treatment is employed.

When the English form of hearth is in use, the refining of the *blicksilber* is carried on in the same furnace as the cupellation for *blicksilber*, the method of working this furnace having been previously described. In many works a similar method is employed with the German hearth, the *blicksilber* being refined on the same hearth on which it was produced, the blast being either cut off after the brightening of the silver or else very much reduced in quantity. The oxidation is then continued until the metal exhibits all the properties of fine silver, viz., a clean, mirror-like surface, entire freedom from spots on samples withdrawn from the bath, and a satin-like and uniform fracture, samples being also assayed in order to check its purity. The oxides which form on the surface of the bath are absorbed by a little marl strewn on it and then raked off.

According to Ohl,[1] the loss of silver does not amount to more than 0·018 per cent., and according to Föhr,[2] the silver obtained at the Victor-Friedrichshütte, near Alexisbad, is 998 fine (99·8 per cent.) At these works the method of muffle refining formerly in use has been replaced by the refining in the German hearth, which has done away with the cost of melting the silver and of preparing the hearth.

Refining in a special reverberatory furnace is the most general method of conducting the process, the English cupellation hearth coming under this head. This method gives the greatest yield for the smallest expenditure of fuel, but is attended with a certain amount of loss of silver by volatilisation. The removal of bismuth is not as complete as in Rössler's method of using silver sulphate. The

[1] *B. u. H. Ztg.*, 1879, p. 274. [2] *Ibid.*, 1885, p. 382.

furnace hearth is either fixed or movable, the furnace in the latter case being practically the same as the ordinary English hearth. Where the hearth is fixed, the roof is usually a movable one, being either an iron hood with a lining of fireclay, or else composed of firebrick blocks bound round with iron hoops.

The hearth is made of bone ash, marl, ashes, fireclay or cement; coal or wood is used as fuel, rarely gas; air for oxidation either simply enters through the working opening or else a tuyere is used.

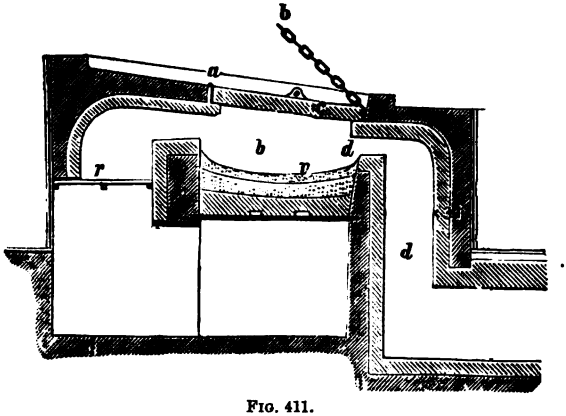


FIG. 411.

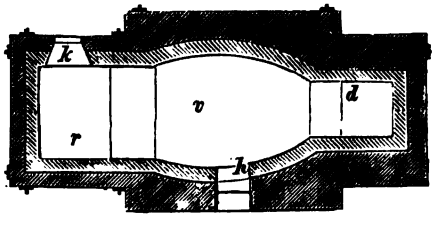


FIG. 412.

Figs. 411 and 412 show a form of refining furnace with fixed hearth and movable cover; r is the grate, b the heating space with cover c and hearth v of marl. The hearth rests on a lower layer of marl resting on the brickwork of the furnace; d is the flue, h the working opening, and k the stokehole.

Furnaces with fixed hearths are first slowly heated for 8 to 12 hours, and then the charge is put in. This is melted down quickly, the door being closed, and a layer of charcoal usually put on top of the silver in order to diminish the loss by volatilisation. The molten

metal is then stirred, and any scum on the surface is raked off, after which air is led over its surface either through the open door or else it is forced in through a tuyere at the fire bridge end.

The oxide formed is absorbed by a little marl strewn on the surface, and when the silver is fine, the blast is stopped, the fire urged, and the molten metal covered with a layer of charcoal in order to prevent "spitting." The metal is then ladled out into moulds, coated with a lime or clay wash, or, if it is to be granulated, run out into vessels filled with water.

Fixed hearth furnaces are in use at Przibram, Freiberg and Lautenthal. At Przibram (Bohemia) 17 to 18 cwt. of blicksilber are put into the hearth, which is of marl, and in 10 hours cupelled up to 996 to 997 fine, 13 cwt. of coal being used. The pure silver (*feinsilber* or *brandsilber*) is cast into 22 lb. bars.

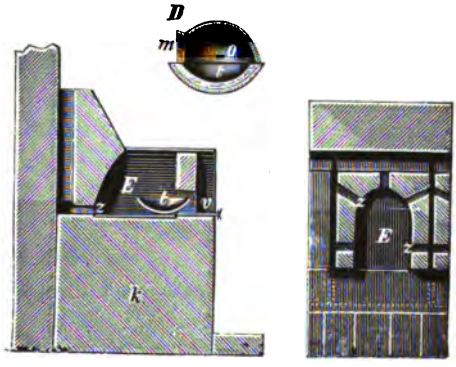
The Freiberg furnace is of similar construction to the Przibram one, the charge consisting of 20 to 24 cwts. of *blicksilber*, the operation lasting 10 to 12 hours, and the coal consumption being 60 per cent. of the weight of the charge. The silver obtained is from 996 to 998 fine, and as it is auriferous, it is granulated to obtain it in a form convenient for the separation of the gold.

The Lautenthal furnace has a movable cover to the hearth made of firebrick, held together by iron hoops. The marl hearth rests on a layer of firebrick, resting in turn on a slag layer, 5½ inches deep, carried by an iron plate. The fire is of coal and faggots, with closed ashpit and blast. There are two nozzles one inch in diameter behind the firebridge, so placed that their axes meet 23¼ inches from the latter, and delivering air at a pressure of about a third of an inch of mercury. If the silver contains copper, some lead is added, which lengthens the time of the operation. The charge consists of from 13 to 14 cwt. of *blicksilber*, 154 lbs. of coal and 10 faggots being required for every 2 cwt. of *blicksilber*.

Refining under a muffle is rarely carried out, as the fuel consumption is high and the silver loss considerable, whilst only small charges can be worked. The muffle is either a movable one, and in that case the hearth is made of bone ash, marl, or lixiviated wood ashes rammed into an iron dish set under a fireclay hood, or else it is fixed, the test being built round with bricks under the furnace roof, and covered with a perforated iron plate coated with clay.

The construction of the muffle furnace with movable test, used in the Lower Harz, is shown in Figs. 413 to 415. The muffle consists of the test pan *t* and the cover *D*, which can be lifted off from the pan. The test pan is made of iron with a lining of marl or lixiviated

wood ashes, and the cover of fireclay. The front of the heating chamber (*E*) is made up with firebricks after placing the muffle in position, leaving only the working opening *v*. The silver to be refined is put in through the opening *m*, through which, also, the air necessary for oxidation enters, leaving it through the slits at *o*. The muffle is heated with carbonised fuel, the necessary air entering partly through the working door and partly through channels, *z*, in the brickwork of the furnace.



FIGS. 413—415.

At Oker the charge for such a furnace is from 50 to 55 lbs. of *blicksilber*, and after this has been put in, the muffle is surrounded with charcoal and the silver melted. The refining lasts 3 hours, the molten mass being stirred from time to time and the scum removed, the temperature being raised for the last half hour.

About 8 cubic feet of charcoal are used for refining.

REFINING IN CRUCIBLES

This method of refining is chiefly used for silver obtained by wet methods and by amalgamation, but recently *blicksilber* has also been refined by Rössler's process.



FIG. 416.

The crucibles used are made of iron (preferably wrought iron) or else of plumbago, the latter being the best.

Iron crucibles are heated in a reverberatory furnace, plumbago ones in a wind furnace with coke or charcoal. Such a furnace is shown in section in Fig. 416, the crucible being placed on a fireclay stand resting on the grate bars. and packed round with charcoal or coke; the crucible is inserted and withdrawn through the opening *x* covered with a hinged lid. The air for combustion is either drawn or forced in below the grate, the

waste gases passing along *w* to the chimney (*v*). As the surface exposed to the air by the molten silver is only small, oxidation is assisted by the addition of saltpetre, or, as in Rössler's process, of silver sulphate, or, in case silver chloride is present as in cement silver, potashes may be added.

At Schmöllnitz, for instance, 246 lbs. of cement silver are melted in a plumbago crucible, with the addition of 1 to 5½ lbs. of potashes in order to decompose any silver chloride, and 5 to 20 ozs. of saltpetre for the oxidation of the copper and antimony. The process lasts about 6 hours and after the lapse of this time the slag is taken off and the silver ladled out.

Rössler's process is based upon the fact that lead and bismuth in silver may be oxidised by acting on the molten alloy with silver sulphate, the latter being decomposed at a red heat into silver, sulphur dioxide, and oxygen, which latter element acts upon the impurities mentioned. Copper is not acted on. The silver to be purified is melted in plumbago crucibles and then covered with a layer of sand; dried silver sulphate is now added and stirred in with an iron rod. Part of the silver of the sulphate goes into the slag; lead is first oxidised and then the bismuth, so that it is possible to obtain the latter metal in only a portion of the slag which can be worked up by itself for bismuth.

At Lautenthal, Frankfurt-on-the-Maine, and Hoboken near Antwerp, the silver is melted in plumbago crucibles in narrow cylindrical wind furnaces, having only a small space between the crucible and the furnace walls for the coke used as fuel. Blast is introduced by means of two openings in the lower part of the furnace. The charge at Lautenthal consists of about 7 cwt. of silver 950 to 980 fine. Instead of sand, a ring of wrought iron is laid on the molten silver to prevent the spirting of the silver sulphate and the corrosion of the crucibles. Through the middle of this ring the silver sulphate is introduced in pieces the size of a hen's egg, and after the boiling has ceased, the bath is stirred with an iron rod. The silver sulphate is decomposed in 20 minutes or half an hour, and then the slag is stiffened by an addition of quartz sand and taken out of the crucible, a second portion of silver sulphate is then added and the process repeated, and then a third, or in the case of very impure silver, a fourth lot is added, the total amount of silver sulphate used being from one and a half times to twice the weight of the impurities.

The slag produced has, according to Hampe, this composition:—

Silica	40·7	Silver oxide	2·05 (= 1·88 per cent. Ag)
Phosphorus pentoxide	0·64	Copper	0·45
Sulphuric anhydride	0·61	Antimony	0·02
Sulphur	0·15	Lime	1·73
Ferrous oxide	13·47	Magnesia	0·25
Alumina	0·43	Potash (K_2O)	0·64
Bismuth oxide (Bi_2O_3)	6·01	Soda (Na_2O)	0·26
Lead monoxide	33·5		

The coke used amounts to 30 to 35 per cent. of the weight of the *blicksilber*. This crucible process has the advantage of occasioning only a slight loss of silver and of collecting the bismuth in a proportionately small amount of the slag.

The products obtained in refining silver are fine silver, test ashes and scums. The fine silver still contains one or two parts per thousand of impurity consisting of copper, gold, platinum, palladium, bismuth, arsenic, lead and antimony.

The *spitting* of silver is prevented by the presence of small amounts of lead and copper, but not by similar amounts of gold. As considerable mechanical loss may occur as the result of the spitting, it is sought to prevent it by making openings into the surface of the solidifying silver with an iron tool, by covering the surface with powdered charcoal, or by melting the silver under a layer of common salt or potassium carbonate. Silver also appears to spit in consequence of the absorption of sulphur dioxide, the metal obtained in the precipitation of the sulphate by metallic iron exhibiting this property, though in this case it can be prevented by an addition of saltpetre after the silver is melted.

The test ash is the hearth material mixed with grains of silver and metallic oxides. The grains of silver are extracted from it and the residue smelted for work-lead. The scums are used for the preparation of bismuth if they are rich in that metal, otherwise they are smelted for work-lead, or, if rich in silver, added to the lead bath in the cupellation hearth; occasionally they are treated in the wet way.

II. The Extraction of Silver by a Combination of Dry and Wet Processes

1. By Conversion of the Silver into a Silver-Lead Alloy

Several ores and smelting products in which the silver has to be converted in a silver-lead alloy are treated in the wet way before

leading them in order to separate some particular constituents from the silver, the silver remaining whilst the other bodies go into solution. On the other hand, silver obtained by precipitation or electrolysis is often leaded in order to obtain it as a lead-silver alloy and to free it from other bodies.

In both cases the operation of leading is carried out in the manner previously described, either by smelting the impure silver or the argentiferous bodies with additions of materials rich in lead, or else by adding the substance to a red hot bath of lead.

A. Processes in which the Silver is not Dissolved

The processes in which the argentiferous material is treated in the wet way in order to separate some constituent before the leading operation, the silver remaining undissolved, are as follows :—

1. Roasting argentiferous lead ores containing blende in order to convert the zinc into neutral sulphate, extracting this with water and smelting the residue in blast furnaces for work-lead. This process is in use at the Sophienhütte at Langelsheim, and at the Juliushütte at Goslar, and has already been described in the section on Lead.

2. Dissolving out iron sulphide from argentiferous and auriferous mattes by means of sulphuric acid, and smelting the residue with materials rich in lead for work-lead and matte. This process is in use at Zalathna in Transylvania, and has already been dealt with.

3. Treatment of a mixture of zinc and lead oxides and argentiferous lead, such as is obtained in the zinc process, or by the decomposition of rich scum by means of steam, with ammonium carbonate or sulphuric acid in order to dissolve out the zinc oxide, the argentiferous residue being then added to a bath of lead in the cupellation hearth. This process is in use at Hoboken near Antwerp, and at Lautenthal, and has already been described under desilverisation by zinc.

4. The Hunt-Douglas process, in which the copper is dissolved out of roasted argentiferous matte as copper chloride, and the residual matte then smelted for work-lead. This process, used at the works at Kansas City, has already been described under wet methods for the extraction of copper.

5. The solution of the copper contained in argentiferous copper and in dead-roasted argentiferous copper mattes by means of sulphuric acid, copper sulphate being produced and the argentiferous residue leaded.

The dissolving of copper out of argentiferous refined black copper is the process used at Altenau and Oker in the Harz; at Freiberg dead-roasted copper matte is extracted in the same way. Both processes, which will now be described in detail, are known as "sulphuric acid extraction" (*schwefelsäurelaugerei*). In each, a previous separation of iron is necessary, as otherwise the copper sulphate produced would be contaminated with ferrous sulphate and would be unsaleable. In the case of the matte this is effected by repeatedly roasting and smelting it, and in the case of the black copper by refining the same.

The Extraction of Silver from Argentiferous Black Copper by means of Sulphuric Acid

In this process the black copper is first refined in order to get rid of iron, cobalt and nickel, it is then granulated and treated with dilute sulphuric acid in the presence of air, the copper going into solution, and the silver remaining in the residue which is smelted in blast furnaces with materials rich in lead.

The refining ("*verblasen*") is conducted in reverberatory furnaces having hearths of brasque when the copper contains lead (Altenau), or if free from lead, in the English reverberatory furnace with quartz sand hearth (Oker). The methods used and the chemical changes occurring are the same as in the ordinary refining process (see Copper). The brasque hearths only outlast four charges, the first being one of 3 tons, and the fourth of 2 tons. In the sand hearth each charge weighs 3·5 tons. At Altenau the refining of 3 tons takes from 13 to 15 hours, of which 10 to 12 are occupied in melting, and only 3 in refining proper. At Oker the entire process lasts 12 hours.

The products are tough-pitch copper, which is granulated direct, and refinery slag. At Altenau the first slags are nickeliferous and are sold to the nickel works, and the slag obtained afterwards is smelted up with galena for work-lead and copper matte. At Oker the refinery slag is smelted together with copper ores.

By this refining, nickel, cobalt, zinc, and especially iron, are removed, so that on subsequent solution in sulphuric acid, the copper sulphate is obtained almost pure and in particular free from ferrous sulphate.

The solution of the copper contained in the refined metal depends upon the power of dilute sulphuric acid to slowly dissolve copper if air be present. In the absence of air the dilute acid does not act upon copper, though, as is well known, hot strong sulphuric acid dissolves copper with evolution of sulphur dioxide. No sulphur dioxide is

evolved when the dilute acid is used, the reaction, according to Rammelsberg, being represented as follows:—

$$Cu + H_2SO_4 + O = CuSO_4 + H_2O.$$

The correct explanation may be that copper sulphate in acid solutions takes up copper forming cuprous sulphate, which latter is oxidised by air in presence of acid to cupric sulphate, the copper sulphate really acting as an oxygen carrier. The reaction is hastened by warming.

Of the various foreign bodies present in the copper, zinc, iron, cobalt and nickel are dissolved by sulphuric acid, and lead is converted into lead sulphate, which being insoluble in dilute acid, remains behind in the residue. Antimony, tin and bismuth are converted into basic salts, and remain principally in the residue. Arsenic partly goes into solution as arsenious acid, and partly remains behind as insoluble arseniates. Antimoniates and arseniates are decomposed by warm sulphuric acid forming antimonic and arsenic acids.

In the residue lead sulphate, arsenic and antimonic acids, lead arseniate, basic antimony, tin and bismuth salts, and copper sulphide will therefore be present in addition to gold, silver, and undissolved copper, whilst the solution may contain sulphates of copper, iron, zinc, nickel and cobalt, as well as arsenic and antimonic acids in small amounts.

The solution of the copper is effected in leaden towers or in wooden vats lined with lead, the granulated copper being placed in layers on a false bottom, and dilute sulphuric acid or acid mother liquors allowed to flow over it either continuously or at intervals. The solvent liquid is warmed either in separate vessels by occasionally passing steam in, or else steam is continually passed into the lead towers in which solution is taking place. The necessary air enters at the bottom of the solution vessel and finds an exit at the top.

At Altenau and Oker, wooden vats lined with lead are employed. They are 5 feet 4 inches high, 35 inches in diameter at the top, and 28½ inches below. Two boards are laid at the bottom of the vat and on these a layer of large pieces of copper is placed, or at Oker copper rods are used; above either, a layer 3 feet high, of granulated copper is placed, about 1 ton in weight. The exit for the solution, which serves also for the entrance of the air, measures 8 inches by 8. Above this solution vessel a lead-lined wooden vessel is placed in which sulphuric acid of 50° B, is diluted with mother liquors (from the crystallisation of the crude or pure sulphate) down to 29° or 30° Beaumé. This liquid, which forms the solvent, is heated to 70° C. by

means of a steam coil of lead pipe, and then is distributed by means of a syphon with a rose on the end, over the granulated copper in the vessel below, every half or three quarters of an hour.

The arrangement of these vessels is shown in Fig. 417, where *P* is the vessel for the solvent liquid with a leaden coil for the steam at the bottom, and *z* is the syphon for running the liquid into the dissolving vat. At the bottom of the latter are the wooden bearers *H*, on which large pieces of copper are placed as a foundation for the granulations with which the remainder of the vat is filled. The liquor flows through the opening *t* at the bottom of the vat.

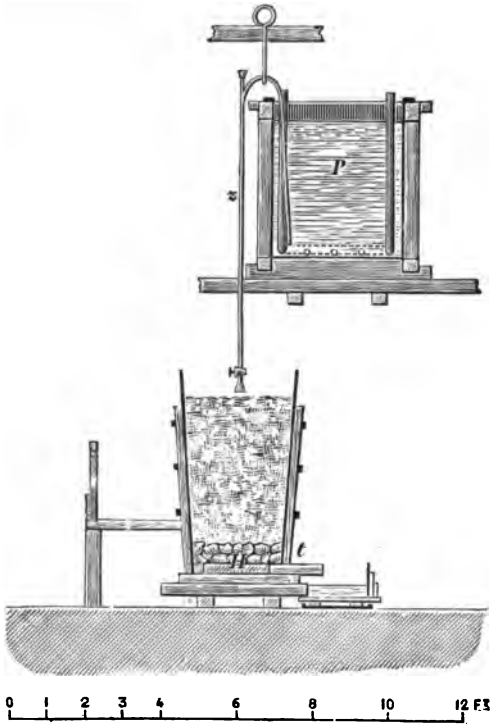


FIG. 417.

The working is conducted as follows:—Solution from the upper vat is allowed to flow through the syphon for 5 minutes over the granulated copper. The granulations become wetted, and under the influence of the acid and the oxygen of the air, copper sulphate is formed and silver slime begins to separate. After an interval of from half to three-quarters of an hour a fresh lot of solution is run on, washing away the copper sulphate and the silver slimes. As soon as clear liquid begins to flow out from the opening below, it is a sign that the copper sulphate and silver slime have been washed out and the flow of solution is stopped, and the action of the still adhering solution and the oxygen of the air is again allowed to proceed. The washing of the granules with the solvent, the so-called spraying or showering ("*bebrause*") only lasts five minutes. After the mass has stood for another half or three-quarters of an hour the spraying operation is again performed; as fast as the granulations are dissolved, they are replaced by fresh ones.

The liquor with its suspended silver slime runs into a long trough having a reservoir for the liquid at the end. In this trough, owing to the cooling and partial evaporation of the liquid, copper sulphate separates in crystals, carrying down with it the silver slimes, the mother-liquor flowing onwards to the reservoir. The mother-liquor is either used for diluting the sulphuric acid (at Altenau), and in this case it is forced up by injectors to the vessel lying above the vats, or else it is used for dissolving the crude sulphate (as at Oker), in which case it flows from the reservoir into a boiling pan placed below

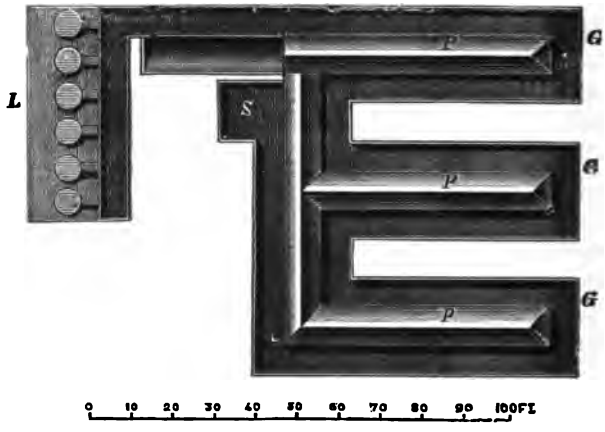


FIG. 418.

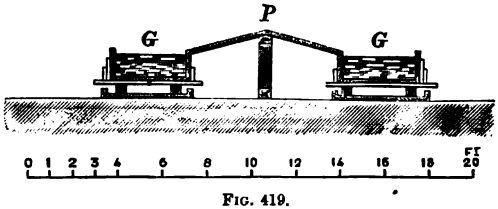


FIG. 419.

it. At Altenau, 8 solution vats deliver their liquor into a lead-lined spout or trough 28 inches broad, 7 inches deep, and 360 feet long; at Oker, 6 vessels deliver their liquors into a similar spout 34½ inches broad and about 345 feet long. The arrangement of the plant at Oker is shown in Figs. 418 and 419, where *L* are the solution vessels, *G* the spout through which the liquid circulates on its way to the reservoir *S*; the channels are placed on each side of sloping lead-covered boards, *P*, as shown in the section in Fig. 419.

The copper sulphate collecting in the troughs and containing all the silver intermixed with it, is drawn on to the sloping boards,

where the crystals drain from adhering mother-liquor. The greater part of the silver is found in the crystals in the first portions of the trough, the quantity diminishing further on. At the end of the trough the sulphate is rich in gypsum, as well as lead arseniate and antimoniate.

The silver slimes are separated from the crystals by treating the crystals with hot mother-liquors in boiling pans, the crystals dissolving in the liquor, and the insoluble slime remaining behind. The boiling pans are of stout sheet lead, supported on cast iron plates, underneath which run flues. The pans are 11 feet 6 inches long, 10 feet 6 inches broad, and 23 inches deep; the mother-liquors are run in first, the liquors from the crystallisation of the market sulphate being used at Altenau, and then if necessary diluted with water down to 18° or 19° B. When the temperature reaches 70° C. crude sulphate is thrown in until the density reaches 28° B., but not higher, otherwise the crystals subsequently obtained would be small and inferior. The slimes are then allowed to settle, the addition of the crude sulphate and the mixing of the same taking about an hour, and the settling 6 to 8 hours. Before withdrawing the liquor from the pan a little pulverulent copper is usually added to precipitate any silver that might be in solution, or else the solution is made to flow through a filter of granulated copper on its way to the crystallising vats. The clear liquid is drawn off into these vats at a temperature of 70° C, and the copper sulphate allowed to crystallise out. At Altenau, the liquor is syphoned out from the boiling pan whilst the slime left behind is transferred to a slime box and there washed, the liquors being again syphoned off after the slime has settled. At Oker, liquid and slime flow into a vessel, which communicates with the bottom of the boiling pan, and which has two openings closed by wooden plugs situated at different heights. The clarified liquors are run off through the upper opening, and the silver slime through the one at the bottom of the vessel.

The crystallising vats are lead-lined wooden vessels, 6 feet 3 inches long, 10 feet 6 inches broad, and 23 inches deep, each vat being capable of holding the contents of a boiling pan. Lead strips, of which there are 25 or 30, hang in the vat, and on these the crystals deposit. The operation lasts from 8 to 12 days, the crystals are then taken out, washed with water to free them from mother-liquor, and then dried for 8 days in drying rooms kept at a temperature of 20 to 25° C.

The silver slimes in the dry state contain from 2 to 15 per cent. of silver, and are leaded, being smelted at Altenau together with *abzug*, litharge and copper matte in such proportions that a work-

lead with 1½ to 2 per cent. of silver, and copper matte with 25 per cent. of copper and 0·5 per cent. of silver, are obtained.

At Oker the slimes are smelted for work-lead, together with zinc scums from the zinc process and anode slime from the electrolytic process, as well as with litharge.

The mother-liquors obtained in the process can be used again for dissolving the granulated copper and the crude sulphate, provided that the copper is free from iron and nickel. Otherwise the sulphates of these metals accumulate in the mother-liquor which must then be withdrawn from the process.

With regard to the yields from the process, at Oker, from 1 cwt. of granulated copper, 418 lbs. of sulphate are obtained, using 176 lbs. of sulphuric acid of 50° B. The capacity of the plant, consisting of 6 solution vessels, 2 boiling pans, and 24 crystallising vats, amounts to 30 cwt. of copper sulphate in 24 hours.

At Altenau, in the year 1887–88, 209·865 tons of granulated copper and 488 tons of sulphuric acid of 50° B. were used, together with 763 tons of coal, and the products were 862 tons of copper sulphate, and 85·5 tons of silver slimes. The 85·5 tons of slimes were smelted with 18·9 tons of litharge, 19·05 of copper matte, 6·15 of limestone, 4·9 of *abzug*, 3·5 tons of Oker extraction residues (from the chloridising roasting and lixiviation of cupriferous burnt pyrites), and 150 tons of slags. The consumption of coke for smelting this amount was 29 tons, and 78·45 tons of work-lead and 28 tons of copper matte were obtained.

The possibility of employing this method of extraction depends upon the price of copper sulphate. If this is high, the process can be profitably worked, and may then pay better than the electrolytic separation.

In order to separate the silver from argentiferous cement copper, the latter is roasted in a muffle furnace in order to convert the copper into oxide, and the roasted material is then treated with dilute sulphuric acid, which dissolves the oxide and leaves behind the silver. This process is employed, for instance, at Hemixem, near Antwerp, where the price of copper sulphate is high.

The Extraction of Silver from Argentiferous Copper Matte by means of Sulphuric Acid

(*Freiberg Sulphuric Acid Extraction*)

In this process, the argentiferous copper matte is concentrated in order to get rid of iron, the matte being then roasted sweet, by which

means the copper is converted into oxide, and the silver into metal; the copper is then dissolved out by means of dilute sulphuric acid, and the argentiferous residue is smelted with lead ores or similar materials in a blast furnace.

This process is in use at Freiberg, and depends upon the fact that copper oxide is easily soluble in dilute sulphuric acid, whilst metallic silver is not affected by it.

The concentrated copper matte of Freiberg contains 69 to 74 per cent. of copper, 3 to 7 per cent. of lead, 0·3 to 0·4 per cent. of silver, 2 per cent. of iron, 3 per cent. of cobalt and nickel, 0·5 to 1 per cent. of antimony and arsenic, and 14 to 19 per cent. of sulphur. It is roasted sweet in a long-bedded calciner, 10 cwt. of matte remaining in the furnace for 16 hours. The mass is then sieved, and any imperfectly roasted material crushed and again roasted. The roasted matte is crushed and then submitted to the action of sulphuric acid in open vertical cylinders of hard lead, 4 feet high and 4 feet to 4 feet 6 inches diameter, provided with exit tubes at the bottom.

The process of solution is begun by bringing into the vessels 4 cwt. of chamber acid of 48° to 50°B., and then diluting this with an equal volume of water or acid mother liquors. The liquid is then brought to the boiling point by superheated steam injected directly into it, and the crushed roasted matte is added in portions of from 2 to 3 cwt., and thoroughly stirred with wooden poles. To dissolve the anhydrous sulphate formed, water or mother liquor is added from time to time, and as soon as the liquor is saturated, which is the case after about 5 hours, the steam is shut off and the liquor allowed to stand for an hour, the silver slime settling to the bottom. The liquor is then syphoned over with leaden syphons into settling vats, and after remaining there for an hour, again syphoned into the crystallising vats, where the copper sulphate crystals deposit on lead strips.

As the crude sulphate may still enclose some silver slime, the greater portion of it is again dissolved and filtered through a linen filter placed on the perforated false bottom of a cylindrical vessel, and covered with a layer of granulated copper. Any silver that may have gone into solution is thus precipitated on the copper, whilst the slimes are retained by the cloth.

The slimes which remain in the first vat are treated with dilute sulphuric acid and steam in a lead-lined pointed box (*spitzkasten*) in order to dissolve any adhering anhydrous sulphate or other soluble impurities, then washed on a cloth filter, and lastly smelted with argentiferous ores for work-lead. The slime contains 1 to 2 per cent. of silver, 5 to 11 per cent. of copper, and about 40 per cent. of lead.

The crystallised copper sulphate is free from iron; crystals containing over 0·035 per cent. of iron are redissolved and recrystallised. The mother liquor from the crystallisation of the first crude sulphate is acid, and is used for diluting the sulphuric acid used in dissolving the roasted matte. When it cannot be thus employed on account of the iron in it, it is treated with metallic iron (after crude sulphate has been repeatedly crystallised out) to precipitate the copper, the liquor remaining being either allowed to crystallise for ferrous sulphate, or used as a binding material in making pyritic smalls into bricks. The mother liquor from the recrystallisation of the copper sulphate is treated in the same way after it has been in use for some time and has become too rich in iron.

The question whether it is more advisable to treat the black copper or the roasted copper matte with sulphuric acid, depends chiefly upon local conditions. The copper matte must undergo several roastings and smeltings in order to free it from its iron content before it can be treated with sulphuric acid, as otherwise the copper sulphate obtained would be contaminated with ferrous sulphate. Compared with this there is the smelting of the roasted copper matte for black copper and the refining of this before its solution.

By comparing the Freiberg process with the black copper dissolving process in use at Altenau in the Harz, Kuhlemann[1] arrives at the conclusion that the economic results of the two processes would be about equal were it not for the fact that at Altenau, owing to the copper containing antimony and arsenic, residues containing these metals remain when it is dissolved in acid, and that in working up such residues there is a greater loss of metal than is the case in the smelting of the Freiberg residue. In addition, the solution of the copper in acid requires a longer time than the solution of the oxide, and more strongly acid liquors are produced.

B. Processes in which the Silver is Dissolved

Silver precipitated from its solutions is seldom pure, and has in consequence to be leaded. This leading is performed by smelting the silver precipitate with materials rich in lead, such as litharge or old cupellation hearths in blast furnaces, or else by adding the precipitate to red hot molten lead, contained either in an iron pot or else in the cupellation hearth.

In this way, silver sulphide precipitated from thiosulphate liquors is leaded in a bath of molten lead, either in the cupellation furnace,

[1] *Preuss. Ministerial-Zeitschrift für Berg. Hütten. und Salinenwesen*, vol. 19, p. 180.

as at St. Andreasberg, or in cast-iron vessels as at Kapnik in Hungary. Silver thrown down as metal by copper from solutions of its chloride is treated in the same way at Kapnik.

Silver precipitated from argentiferous copper liquors as sulphide, or as iodide subsequently converted into sulphide by treatment with sodium sulphide, is usually leaded by smelting with materials containing that metal in blast furnaces. The processes in which silver is dissolved and then precipitated will be considered subsequently.

2. The Extraction of Silver by the Amalgamation Process

In the amalgamation process, the silver in ores or metallurgical products is converted into a mercury alloy or amalgam, which is subsequently distilled, the silver being left behind and the mercury condensed and used over again. The mercury is used in the metallic state, its employment in the form of soluble salts (mercuric chloride, as in Designolle's process) not having proved a success.

The amalgamation process has the advantage of requiring but little fuel, and with suitable ore gives a high percentage of extraction. There are, however, the disadvantages of a considerable loss of mercury and incomplete extraction in the case of pyritic ores, or ores containing blende, lead, arsenic, antimony and bismuth compounds. The process is best adapted for use with a certain class of ore (native silver, with chloride or sulphide, free from lead and from any tough clayey gangue), where mercury can be had cheaply, and where fuel is dear. Such conditions chiefly prevail in parts of America, and under these circumstances the process is a better one to employ than either the smelting process or the wet extraction. There are two principal operations in the amalgamation process:—

1. The production of the amalgam.
2. The separation of silver from the amalgam.

1. The Production of the Amalgam

Mercury unites directly with native silver, forming silver amalgam. Silver chloride is easily decomposed by mercury with the formation of mercurous chloride and free silver, which then unites with the excess of mercury; iodide and bromide of silver are also decomposed by mercury but not so readily as the chloride. Silver sulphide is slowly decomposed by mercury with the formation of mercuric sulphide, the decomposition being more rapid in presence of iron, and especially on heating. Arsenical and antimonial compounds of silver are only slowly and incompletely decomposed by mercury alone

It is not therefore possible to extract the silver from most ores and metallurgical products by simple treatment with mercury, only those ores containing their silver either free or as chloride being capable of amalgamation without further treatment. The decomposition of silver chloride by mercury is always attended with a loss of mercury owing to the formation of mercurous chloride, so that it is preferable in most cases to bring about the decomposition of this compound by means of metallic iron or copper.

Ores containing silver as sulphide are only very slowly attacked by mercury, with the formation of mercuric sulphide. They are, therefore, treated with mercury and metallic iron, or with copper chloride and mercury, either alone or together with iron, copper, lead or zinc, or else the silver in the ore is converted into chloride by roasting with salt, and the roasted ore is then treated with mercury and iron or copper. In every case the silver is reduced to the metallic state, and amalgamates with the mercury, which must be present in excess.

Ores and metallurgical products containing silver sulphide, together with other metallic sulphides, particularly those of arsenic and antimony, are also treated with copper chloride and mercury, or with copper chloride together with iron, copper, lead or zinc, and mercury, or else they are roasted with salt and then treated with iron or copper in presence of mercury. By these methods the silver is separated in the metallic state, combining then with the mercury present to form amalgam.

The processes can consequently be divided into those where the amalgamation is effected by the action of mercury alone, and those in which reagents are employed in addition. These reagents either assist the action of the mercury upon silver sulphide, as is the case with iron, or they liberate metallic silver from its chloride (copper, iron, zinc, lead), or they convert the silver present as sulphide, or as an arsenic or antimony compound, into metallic silver or its chloride.

The processes in which reagents are used can again be divided into those where amalgamation takes place without any preliminary chloridising roasting of the ores or metallurgical products, and into those where the amalgamation is preceded by a chloridising roasting.

Amalgamation processes may consequently be classed under three heads :—

1. Amalgamation with mercury alone.

2. Amalgamation with mercury and certain reagents without roasting.

3. Amalgamation with mercury and reagents after a chloridising roasting.

In every case it is essential that the ores or metallurgical products should be in the state of fine powder, and should not contain any admixtures which would coat the silver particles with a tough pasty mass, liable to mechanically retain particles of mercury. Clay and certain magnesium silicates form such objectionable masses.

In order that the mercury may react properly, it must have a bright clean surface, be finely divided, and be brought into intimate contact with the powdered ore. The action of the mercury is greatly hindered by its globules becoming coated with a layer of calomel, clay, oil or grease, and these must be removed by chemical or mechanical means. The affinity of the mercury for the ore powder to be amalgamated is increased if it contains small quantities of silver, zinc, copper or lead, but large amounts of these bodies, especially of lead, have an injurious influence.

Of the various metals that may be present, gold is the most easily amalgamated, even more readily than silver itself. Zinc, lead and bismuth are also easily amalgamated, and copper, if in a state of fine division, but not at all readily if in large pieces. Arsenic and antimony are only amalgamated with difficulty, iron, nickel and cobalt not at all.

The losses of mercury during amalgamation are partly chemical and partly mechanical. The chemical losses are due to the formation of mercurous chloride and mercuric sulphide by the reaction of mercury with silver chloride and sulphide, or else arise through the production of mercurous chloride due to the action of cupric and ferric chlorides upon mercury. This latter source of loss can be avoided by the addition of iron, which reduces the two chlorides to the cuprous and ferrous compounds.

The mechanical losses are due partly to the *flouring* of the mercury, partly to losses of portions of mercury and amalgam which remain behind in the residue.

The *flouring* of the mercury is the result of its division into minute globules, which cannot be made to unite together into drops, and are in consequence washed away by the water, and it is caused by the too rapid rotation of the amalgamating apparatus, the little globules of mercury thus formed being prevented from coming together again by the earthy or clayey matters present.

The losses owing to mercury remaining behind in the residues, arise through particles becoming coated with tough clayey masses

and also as a result of the imperfect separation of the mercury from heavy minerals, lead ores in particular acting injuriously in this way.

1. AMALGAMATION WITH MERCURY ALONE

This method, known as direct amalgamation, is used in the case of ores which contain chiefly native silver with smaller quantities of sulphide or chloride. It is sometimes combined with other methods of amalgamation, the ores being first treated with mercury alone in order to extract the native silver and any gold present, and the residue being then submitted to a chloridising roasting in order to convert the sulphur, arsenic or antimony compounds into chlorides.

The process consists in rubbing the ores with mercury, the crushing of the ore either going on at the same time or having been done previously. The ore is more generally crushed first and then the amalgamation is conducted in iron pans. Mills with revolving crushers of stone (Arrastras) and edge runners (Chilian mills) are employed for the simultaneous crushing and amalgamation of the ore.

This method of amalgamation was formerly employed in Peru, Chili and Mexico, and is still employed in some localities in these countries where the necessary ore can be procured.

The Peruvian process, known as the Tintin process, was described by Alonzo Barba in 1640.[1] The apparatus used consists of a hard stone with a cavity 9 inches wide and 9 inches deep, the ore in small pieces being triturated with mercury and water in this cavity by means of an iron pestle, water being kept flowing continually into the cavity at one side and out at the other. This water runs into tanks and deposits its suspended particles, and as these may contain arsenic, sulphur or antimony compounds of silver, they are further treated by the Patio process described later on.

In Chili, large quantities of ore containing chiefly native silver, but carrying also chloride, chloro-bromide, bromide and iodide of silver, as well as native amalgam (arquerite), were treated by the direct amalgamation process. These ores were found in the upper portions of the ore deposits in the Copiapo valley, and were known as *metales calidos*, in contradistinction to the ores from the deeper portions of the deposits, consisting of sulphur, arsenic and antimony compounds, unfit for treatment by direct amalgamation, and known as *metales frios*.

[1] Percy, *Silver and Gold*, p. 563.

The ores were first crushed in edge runners (Chilian mills) from 4 to 6 feet in diameter, constructed usually of stone with an iron rim, and were then submitted to the amalgamation process in tubs or vats known as *tinas*, similar to those represented in Figs. 420 and 421. The sides were of wood, the bottoms of cast iron, and on the upright shaft *m*, two wrought iron arms were attached just touching the bottom and serving to bring the mercury into intimate contact with the ore, these agitators being rotated by bevel wheels, as shown in

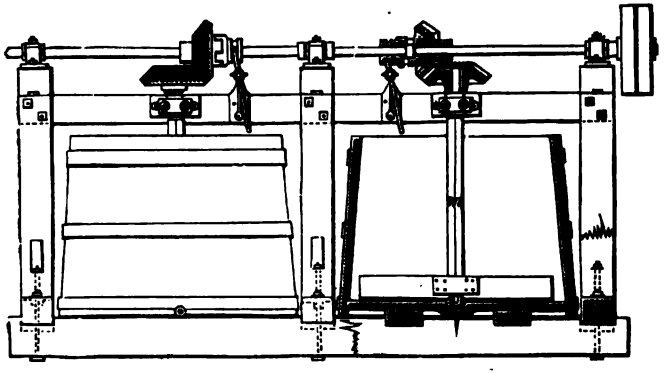


FIG. 420.

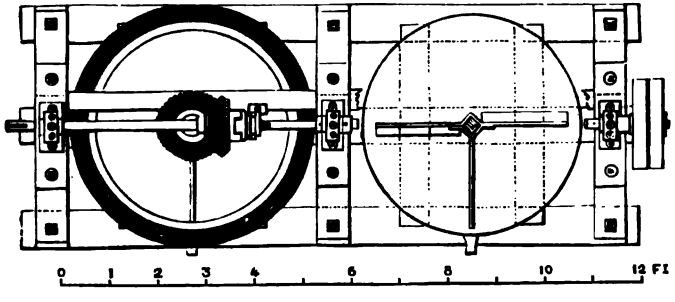


FIG. 421.

the figure. At the bottom of the *tina* was a hole closed by a wooden plug for the purpose of drawing off its contents.

The charge for each *tina* was from 4 to 6 cwt., depending on the character of the ore, and 150 lbs. of mercury were used for poor ores, and more for richer ones. The rubbers made about 16 revolutions per minute, and the amalgamation lasted 4 to 6 hours with ores containing only native silver, or about 20 hours when silver chloride or chloro-bromide was present. This is owing to the greater difficulty of bringing chloride of silver into contact with the mercury,

the grains being flattened during grinding, and having a tendency to remain suspended in the water.

After the amalgamation had proceeded for a sufficiently long time, the amalgam was drawn off through the hole at the bottom into an iron pot, after which the entire contents of the *tina* were run into settling tanks, in which the solid matter was deposited. The amalgam was first drained from excess of mercury in canvas



FIG. 422.

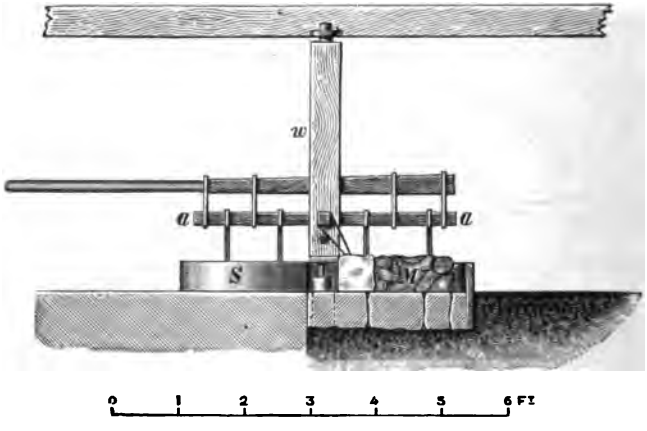


FIG. 423.

bags, and then pressed into iron moulds, the pressed amalgam containing from 16 to 25 per cent. of silver.

In Mexico, ores containing native silver, together with a small amount of sulphide, were first stamped in mills and then amalgamated in *arrastras*, a special kind of mill.

The *arrastra* shown in Figs. 422 and 423 consists of a circular floor of hard stones set on edge, varying in diameter from 5 feet to 11 feet 6 inches, and surrounded by a raised rim, 12 inches deep, of stone or

blocks of wood. A vertical shaft *w* is fixed in the centre, provided with arms *a*, to which the heavy mill-stones *M* are attached by cords or chains. The axle is revolved by water or mule power, and the ore is further crushed by the revolving stones, and brought into intimate contact with the mercury that is added. Any gold or silver is amalgamated by the mercury, and sulphide of silver is decomposed with the production of mercuric sulphide.

At the works at Batopilas, a town in Southern Chihuahua, Mexico,[1] the ore is first crushed in a stamp battery and from the stamps it drops on to a screen with $\frac{5}{8}$ inch slits, whereby the larger lumps of silver are separated and remain on the screen. These lumps are refined along with the retort silver, whilst the ore passing through the screen is amalgamated in *arrastras*. The charge for each *arrastra* is about a ton of ore, and about 25 lbs. of mercury are added at intervals during the grinding which occupies about 8 hours.

Every morning, a sufficiency of water is put into the *arrastra*, and the grinding continued for 4 to 6 hours, when part is run off, carrying with it a certain amount of the finely-ground and desilverised ore suspended in the liquid. Rich ore is added in place of that drawn off, and a corresponding amount of mercury (25 lbs. per ton of ore), and after three days' working in this way the amalgam is scraped up, and washed in wooden bowls, with the addition of about 10 per cent. of mercury. The slimes produced, which are rich in silver, are concentrated by washing on tables. The amalgam is squeezed into balls 2 inches to $2\frac{1}{2}$ inches in diameter in canvas cloths, in order to free it from excess of mercury, and is then retorted.

Instead of this method of amalgamation, the pan process described below is now adopted at Batopilas. According to the present state of metallurgical knowledge, the pan treatment affords the most satisfactory means of working the amalgamation process where mercury is used alone. This is described in detail under the name of the Washoe process.

2. Amalgamation in Presence of Reagents, but without Previous Chloridising Roasting

This method is generally used when the silver exists in the form of sulphur, arsenic or antimony compounds, or of simple sulphide, or in the form of haloid salts, the reagents being added in the amalgamating apparatus.

[1] Percy, *Gold and Silver*, p. 574.

The processes included under this heading are the Cazo, Kröhnke and Patio processes, and the Washoe or wet process of pan amalgamation. The Washoe process is the most generally used, and is the one most to be recommended with suitable ores.

The Cazo Process

This process, known also as the Caldron process, or the hot pan amalgamation process, is applicable to ores containing native silver and horn silver. It is conducted in vessels made either wholly or partially of copper, and the reagents are the copper of the amalgamating vessel or the agitators, and a boiling solution of common salt. The silver chloride in the ore is decomposed by the metallic copper, and the liberated silver is then taken up by the mercury. The cupric chloride formed is converted into cuprous chloride by contact with metallic copper, the cuprous chloride dissolving in the hot salt solution. Any native silver present is taken up directly by the mercury.

This process was devised in 1609 by the priest Alonzo Barba, of Peru, and practised in South America and Mexico for the working of ores containing horn silver, occurring in the upper layers of the ore deposits. As the mines increased in depth, silver chloride gave place in great measure to sulphur, arsenic and antimony compounds, and in consequence the Cazo process has been abandoned at most places. The yield of silver by this process was very good. The loss of mercury varied from 2 to 2½ times the weight of the silver in the ore.

The ores were first crushed in stamp mills, and then in *arrastras*. They were then concentrated if not sufficiently rich (½ per cent.) by washing on concave tables (*planillas*), the residues, if sufficiently rich, being treated by the Patio process.

The amalgamating vessels used at first were small and known as *cazos*, but afterwards, and particularly in Mexico, larger vessels called *fondones* were employed. The *cazo* was originally made entirely of copper, but later, wood or masonry vessels with copper bottoms came into use. The dimensions of such a vessel were:[1] diameter at the top 3 feet 3 inches; at the bottom, 2 feet; height, 18 inches; the copper bottom was 2 to 2½ inches thick. The vessel was placed over a fire without grate or chimney, the charge for such a vessel consisting of 1 cwt. of ore. This was stirred up in the *cazo* with water to a thin pulp, the mass raised to the boiling point, and then common salt added in quantities of from 5 to 15 per cent. of the weight of the ore. In order to prevent the salt caking on the bottom, it had to be kept stirred until the liquid was boiling.

[1] Egleston, *Metallurgy of Silver, Gold and Mercury*, vol. i., p. 313.

After the salt was dissolved, mercury was added in separate portions, the whole contents being stirred with a wooden stick during the addition. It was usual to add at first a quarter of the entire amount of mercury to be used, and the second quarter after half an hour, or as soon as the amalgam had the appearance of a bright grey sand, further additions being made until the amalgam contained 2 parts of mercury to 1 of silver. This extended over 6 hours, and the fluid in the vessel was then ladled out and used again for the next amalgamation. The solid mass containing the amalgam was then taken out with wooden bowls, and washed in large wooden dishes, with the addition of about as much mercury as had already been used in the amalgamation.

One important point in the amalgamation was to prevent the mercury adhering to the copper. Not only was the process of amalgamation thus hindered, but a loss of mercury occurred owing to the reaction with silver chloride, and the production of mercurous chloride. It was found that if the proportion of mercury to silver was as 2 : 1 such adhesion never took place, but it was not to be prevented if more than 4 parts of mercury were present to 1 of silver.

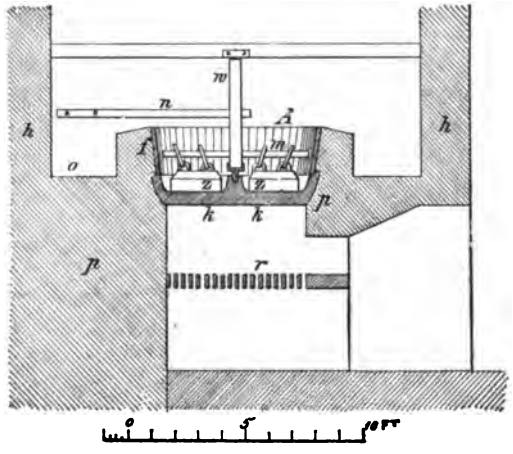


FIG. 424.

The larger vessels called *fondones* were 7 feet in diameter at the top, 6 feet at the bottom, and 2 feet 9 inches high. The bottoms were cast of copper, 7 to 7·8 inches thick, 7 inches deep, and 6 feet in diameter. On the turned up edge of the bottom was built a vessel composed of wooden staves 27½ inches long, and bound round with iron hoops. Resting on the copper bottom and fastened to two arms attached to a vertical shaft were two cast copper blocks, each 300 lbs. in weight, which could be driven round by mules. The *fondon* was heated by a fire-grate below it.

Such a *fondon* is shown in Fig. 424, where A is the vessel with copper bottom, *k*; *f* are the wooden staves, *z* the copper blocks fastened

to the arms *m* of the vertical shaft *w*. The shaft is driven round by mules attached to the arm *u*, and walking round in the space *o*; *r* is the fireplace, and *p* the brickwork.

The charge for a *fondon* was from 10 to 12 cwt. of rich ore. This was charged in with sufficient water to make a thin mud, the gear set going and the fire lighted. As soon as the water boiled, from 10 to 25 per cent. of salt was added, according to the percentage of silver in the ore.

The agitator made about 10 revolutions per minute, the mercury being added in separate portions as in the *cazo*, the first addition being equal to half the weight of the silver present. The process lasted about 6 hours, and after the lapse of this period, the liquid and the lighter portions were run off through a side opening, whilst the heavier portions and the amalgam lying on the bottom were scooped out and washed with the addition of more mercury. The portions washed away, if at all rich in silver, were treated by the Patio process.

If the mercury was added in too great excess or the agitators revolved too slowly, the mercury adhered to the copper, delaying the process and causing a loss of mercury. The loss of mercury ordinarily amounted to 2 per cent., part of it being mechanically lost and part volatilised.

The Kröhnke Process

The Kröhnke process was introduced into Copiapó in Chili, in 1860, by the then German consul of that name, and consists in the employment of a hot solution of cuprous chloride in common salt to decompose the silver compounds, which are then reduced by means of zinc or lead used in the form of an amalgam of these metals. In this method, the production of ferric and cupric chlorides is prevented, and the loss of mercury owing to the formation of mercurous chloride is thus avoided. Lead and zinc also prevent the action of mercury on silver chloride, these metals reacting upon silver chloride with the formation of lead and zinc chlorides, and metallic silver. Not only is the loss of mercury through chemical reactions prevented, but the mechanical loss is lessened, as mercurous chloride, which would be formed were these metals not present, would coat the globules of mercury, prevent their coalescing and give rise to loss owing to flouring of the mercury. The silver formed by the action of the lead or zinc, as well as that present in the ore in the free state, is taken up by mercury and obtained as an amalgam.

Metallurgical opinion is divided upon the question of the chemical reactions occurring in the process, particularly as regards the question

of the amount of silver chloride produced, and of the reduction of metallic silver from silver sulphide or mixed sulphides, without previous formation of silver chloride.

According to the latest researches of Rammelsberg,[1] silver sulphide is decomposed by cuprous chloride in the following way :—

$$Ag_2S + Cu_2Cl_2 = 2AgCl + CuS + Cu,$$

the silver according to this equation being completely converted into chloride.

According to Laur's researches,[2] cuprous chloride in presence of mercury reacts with silver sulphide, with the production of silver without any previous formation of choride, the equation being:

$$Ag_2S + Cu_2Cl_2,NaCl = CuS + 2Ag + CuCl_2,NaCl.$$

According to Eich, cuprous chloride in presence of zinc causes the separation of metallic silver from silver sulphide in this way:

$$Ag_2S + Cu_2Cl_2 + Zn = 2Ag + Cu_2S + ZnCl_2,$$

the reaction proceeding very quickly if mercury be present in addition to the zinc.

By the action of cuprous chloride on pyrargyrite, a part of the silver is set free according to Rammelsberg, silver sulphide and chloride being formed at the same time, according to the equation:

$$2Ag_3SbS_3 + Cu_2Cl_2 = 2AgCl + Ag_2S + 2Ag + 2CuS + Sb_2S_3.$$

According to Eich, a hot solution of cuprous chloride in common salt acts on pyrargyrite as follows:

$$3Ag_2S,Sb_2S_3 + 3Cu_2Cl_2 = 3Ag_2S + 3Cu_2S + 2SbCl_3.$$

Cuprous chloride in presence of zinc or lead is said thus to cause the separation of metallic silver from silver sulphide, and according to the above somewhat contradictory researches, the formation of silver chloride, together with metallic silver, is quite possible. Silver chloride is decomposed by zinc, and a portion of the silver sulphide may also be decomposed by means of zinc and mercury.

It is impossible to say to what extent silver chloride is produced by the action of cuprous chloride, metallic silver is reduced by the action of cuprous chloride in the presence of lead or zinc and mercury from simple and complex sulphur compounds of silver, or metallic silver is formed by the action of zinc upon silver sulphide, because the process is kept secret, and no investigations upon it have been published.

[1] Percy-Rammelsberg, *Silber und Gold*, p. 115.

[2] "Métallurgie de l'Argent au Mexique," *Ann. des Mines*, Séries 6, vol. xx.

But though the reactions are not known with certainty, there remains the fact, that by this process, nearly the whole of the silver in the ore may be converted into silver amalgam.

The process has been used at Copiapó and Antofagasta since 1862, and is suitable for all silver ores except argentiferous copper pyrites, argentiferous galena or zinc blende, and ores containing more than 1 per cent of free arsenic. The loss of silver when antimony, sulphur and arsenic compounds of silver are present with only moderate amounts of galena, zinc blende and pyrites, should not be more than 2 per cent., the loss of mercury varying from 12 to 35 per cent. of the silver obtained.

The amalgamation is carried on in horizontal rotating barrels, having a capacity of from 1 to 4 tons, the 4 ton barrels being 6 feet long, and 5 feet in diameter, with staves 3 inches thick.

The cuprous chloride is made from copper sulphate, salt and metallic copper, salt being added to a copper sulphate solution of 20° B. until it ceases to dissolve. The two salts react with the formation of cupric chloride and sodium sulphate, and the cupric salt is converted into cuprous by the action of scrap copper upon it, the reaction being carried out in wooden vessels and the liquid heated by steam at 3 atmospheres pressure. The cuprous chloride which is only very difficultly soluble in water, dissolves easily in the salt solution. The reduction of the cupric salt to cuprous is shown by the disappearance of the green colour of the solution and by the white precipitate produced on the dilution of a sample of the solution with water. The solution is decomposed by the oxygen of the air with the formation of an oxychloride, and consequently it must be used soon after it is made.

The ores worked in the Copiapó district by this process contain native silver, horn silver, proustite, pyrargyrite, polybasite and silver glance, the gangue consisting of limestone, marl, diabase porphyry, heavy spar, gypsum, asbestos and kaolin. At Escobar and Ossa, the ores are first crushed between two sets of rollers placed one below the other and then finely ground by edge runners (Chilian mills). The arrangement of a so-called Chilian mill or *trapiche* made by Fraser and Chalmers of Chicago, is shown in Fig. 425. The rollers are of cast-iron with steel rims and the bottom of the mill is of steel plate, and the mill is run with a continuous supply of water. The rollers at Copiapó are 6 feet 6 inches in diameter, weigh 4 tons each, and make 10 to 12 revolutions per minute. The finely-powdered ore suspended in the water is run into 2 slime boxes, 15 feet long, 6 feet broad, and 3 feet deep, where it is allowed to settle. As soon as a

box is full the slime is taken out and spread on a flat surface (*cancha*) to dry.

The dried slime is then transferred to the amalgamating vessels which are provided with an agitating arrangement, the exact construction of which is unknown. Hot salt solution containing salt equal to 5 per cent. by weight of the ore is added in quantity sufficient to form a thin pulp, and then the solution of cuprous chloride in common salt is put in. The amount of the latter solution depends both upon the amount of silver compounds present and also upon the nature of the gangue. Ores containing limestone

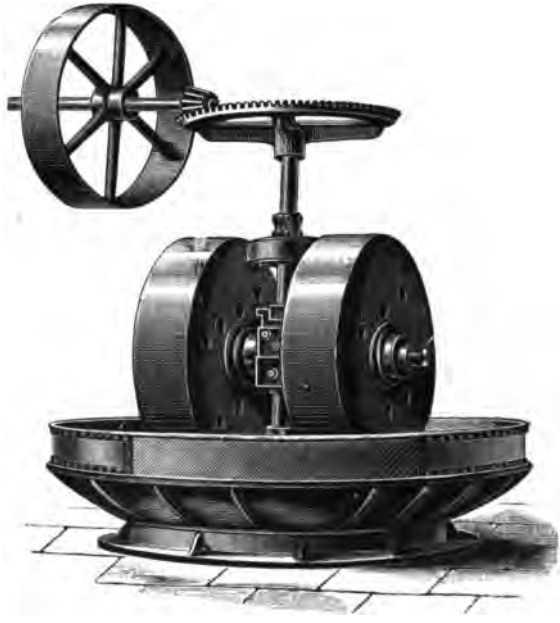


Fig. 425

require more cuprous chloride than ores containing clay or oxide of iron, as limestone partially decomposes cuprous chloride. On an average, with ores of medium richness (0·2 per cent. of silver) and with a mixed gangue, 4 to 5 gallons of cuprous chloride solution are added to a 4 ton charge. After the addition of the cuprous solution the vessel is rotated for 20 to 30 minutes and then mercury and lead or zinc amalgam are added. The amount of mercury added is from 20 to 25 times the silver content of the ore. According to Richter and Hübner[1] lead should be used in the case of kindly ores, zinc being

[1] *Preuss. Zeitschr.*, 1876, vol. 24, p. 487; vol. 27, p. 158.

employed when difficultly decomposable sulphur compounds are present. According to Fonscoa 23 parts of lead should be added for every 100 of silver present in the case of ores containing considerable amounts of chloride and bromide of silver, and in this case the consumption of mercury may be diminished from 150 to 25 parts for this quantity of silver.

After the mercury and lead or zinc amalgam have been added, the amalgamator is run for 6 hours, making 4 to 5 revolutions per minute. A large amount of water is then added and the vessel is again rotated for a short time, when the contents are emptied in a similar way to that employed in the European barrel amalgamation process.

The amalgam obtained contains cupric oxide derived from the action of limestone on copper chloride, as well as copper sulphide, resulting as shown in the preceding equations from the action of cuprous chloride on silver sulphide. The sulphide and a portion of the oxide, as well as mechanically-mixed earthy impurities, are separated from the amalgam by washing with water. For this purpose the amalgam is mixed with 10 per cent. of mercury in a vat (*tina*) provided with agitators (*see* p. 615), and washed with water. the agitators being revolved at the rate of 16 turns per minute until the outflowing water becomes clear. In order to get rid of copper oxide the remaining amalgam is now treated in the same vessel with a solution of ammonium carbonate, in which the oxide is soluble, the solution containing the salt in quantity equal to 2 per cent. of the weight of the amalgam.

If large amounts of copper are present, the amalgam is treated with hot cupric chloride solution. The copper is dissolved, forming cuprous chloride soluble in the salt solution, and lead and zinc are removed in a similar way. The amalgam is then filtered. The mercury removed by filtration is used afresh for amalgamation, until after being in use for 5 or 6 operations it begins to amalgamate very slowly. It is then *quickened* by the addition of 0·02 per cent. of sodium amalgam.

The rich amalgam is pressed in cylindrical cast-iron moulds and then distilled in a bell retort, and the residual silver refined in a reverberatory furnace. The silver thus obtained contains 0·2 to 0·4 per cent. of copper.

For the working of 8 tons of ore every 24 hours, 2 Chilian mills are required using 6 horse-power, 2 slime reservoirs, 2 amalgamating barrels requiring 8 horse-power, a vat for washing the amalgam, a vat for collecting the floured mercury, a vat and steam boiler for

preparing the cuprous chloride solution, 2 vats for dissolving the copper sulphate, and a cement tank for the preparation of the salt solution, with boilers for supplying steam to the same.

The process has proved very successful in Chili, and on account of its quick returns and of the small loss of mercury and silver with suitable ores, should supersede all other processes.

The Patio Process

In this process, which is also known as American heap-amalgamation, the finely crushed and moistened ore is made up into heaps after being intimately mixed with salt, copper sulphate and mercury, and in the reactions which take place, the greater part of the silver, whether present as simple sulphide, as mixed sulphides or as a sulph-arsenide, or sulph-antimonide, is converted into silver amalgam. The amalgam is separated by washing, and is filtered, pressed and distilled.

Though the actual chemical reactions occurring in the process and the extent to which they take place, may not be accurately known, yet this much is certain, that salt and copper sulphate react forming sodium sulphate and cupric chloride. The copper chloride to a certain extent chloridises the silver in simple and complex sulphur compounds, and is partly reduced to cuprous chloride by the action of metallic silver, mercury, copper or cuprous sulphide. This cuprous chloride dissolves in salt solution as in the Kröhnke process and partly acts as a chloridising agent on the silver sulphide or on the mixed sulphides or on silver itself, and partly reduces metallic silver in the presence of mercury from silver sulphide or mixed sulphides. The chloride of silver thus formed is then decomposed by mercury with the production of mercurous chloride. Metallic mercury also reduces silver from some of the silver sulphide with the formation of mercuric sulphide. The separated silver, as well as any native silver present, is then taken up by the excess of mercury present, forming silver amalgam.

The Patio process was first introduced and worked on a large scale in 1557 in Mexico by Bartolomé de Medina, a miner of Pachuca. It was introduced into Potosi in Peru in 1571 by Pedro Fernandez de Velasco. According to a report by Luis Berrio de Montalvo, addressed to the Viceroy of Mexico, and printed in Mexico in 1643, Medina derived his information, that silver could be obtained from its ores by means of mercury and salt, from Spain. Indeed, a similar process was known in Europe before this time, as in a treatise by Biringuccio,

published in Venice in 1540 under the title *De la Pyrotechnica*, it is stated that silver could be obtained from its ores in the wet way by the action of sulphate of iron, verdigris, mercuric chloride, salt and vinegar.

The Patio process is extensively used in Mexico, and is still in use at various South American works. Though the extraction of silver by its means is slow and is attended with considerable loss of mercury, yet it possesses the advantage that the amalgam can be obtained without the expenditure of any fuel, and using animal power only. Consequently it is the only method which can be successfully used in many places in hot climates, where, as in many districts in Mexico, there are no easy means of communication, and where fuel is excessively costly. Until a few years ago, three-fourths of the silver produced in Mexico was obtained by this method, though there is no doubt that, as better means of communication are introduced the Patio process will gradually be replaced by the pan-amalgamation process, or, where lead ores are present, by smelting processes.

Two essential points in the conduct of this process are, that the ores should be of a proper kind, and that they should be in a state of the finest possible division.

The most suitable ores are those which contain native silver and silver sulphide, and are free from iron and copper pyrites, bournonite, galena and blende. The silver glance must be present in a finely-divided condition, as otherwise, it would be beaten out into thin plates in the crushing process on account of its malleability, and such plates would not be readily amalgamated.

Next in order of suitability come the compounds of silver sulphide with other metallic sulphides—pyrargyrite, stephanite, polybasite, proustite, the latter being more difficult to work than pyrargyrite. Argentiferous mispickel and arsenical fahl-ore are not suitable for the process, neither are argentiferous galena, blende and bournonite, zinc blende decomposing cupric chloride with the production of zinc chloride and copper sulphide.

Only such argentiferous copper and iron pyrites can be worked as are capable of oxidation by long exposure to the air, after having been moistened with salt solution.

Native horn silver is much more difficult to amalgamate than artificial silver chloride, and this holds especially in the case of native bromide and iodide. Ores containing haloid salts of silver are in consequence not treated by the Patio process, but by the Cazo or Fondon process previously described.

As regards the amount of silver in the ores, those containing

0·1 per cent. of metal can still be remuneratively worked in Mexico; the richer ores treated by it contain 0·3 per cent. of silver.

In many cases, pyritic ores or those carrying blende, are previously calcined, in order to secure a better amalgamation. Arsenical and antimonial ores must not be roasted, as arseniates and antimoniates, both difficultly amalgamable silver salts, are thereby produced.

The Patio process comprises four operations :—

1. The crushing of the ores.
2. The treatment of the powdered ore in the Patio.
3. The separation of the amalgam produced.
4. The treatment of the amalgam.

1. The Crushing of the Ores

The ores undergo a preliminary crushing in Chilian mills, stamps, rolls, or rock crushers, and are afterwards reduced to powder in *arrastras*. Where the ore is auriferous, mercury is added to the contents of the *arrastra*, in order to collect the gold and any native silver that may be present.

The crushing is usually carried out by means of edge runners (Chilian mills), stamps, or more rarely by crushing-rolls. The old Chilian mills had a cylindrical wheel-shaped granite runner, six feet in diameter and sixteen inches broad, weighing three or four tons. This was fastened to a horizontal arm connected with a vertical shaft, driven by mule power, and revolved on a bed of hard stone. The later forms have cast iron rollers, with rim and bed-plate of steel, and are driven by horses, mules, or by water or steam power. The rollers of such mills are five feet four inches in diameter and fifteen inches broad, with an iron or steel rim four inches thick, their construction being shown in Fig. 425.

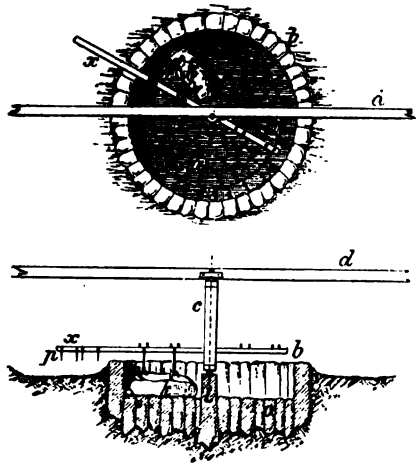
The ore is usually crushed in the dry condition. If stamps or rolls are used they are of the ordinary type, driven either by water or steam power.

At Fresnillo, in Mexico, rolls worked by steam are used instead of stamps, the upper rollers being 18 inches long and 22½ inches diameter, whilst the lower rolls are equal in length, and 27⅛ inches in diameter.

The crushed ore is then finely powdered in *arrastras*, the construction of which has been previously described. In spite of the drawback of their very slow working, no substitute for them has up to the present been found; and this part of the operation is of the

greatest importance, as the yield of silver depends essentially upon the degree of fineness to which the ore is crushed.

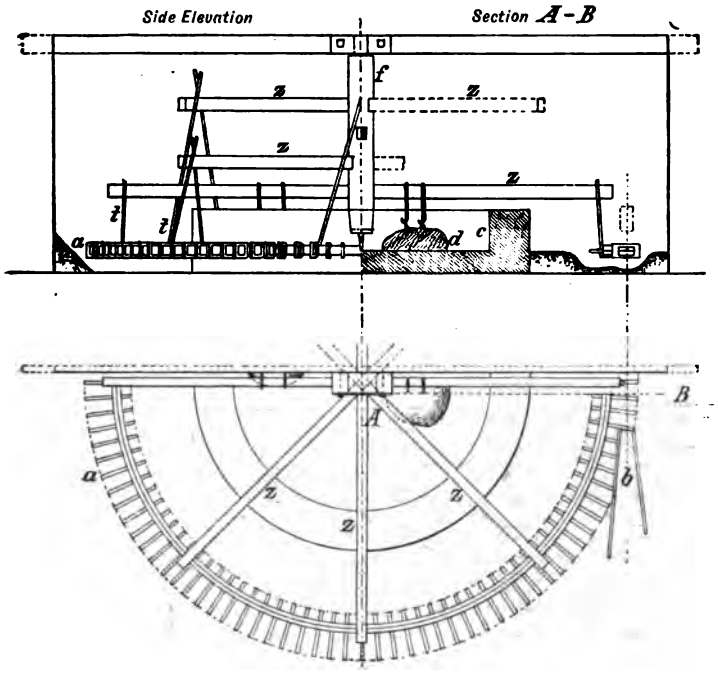
The floor of the *arrastra*, which varies from 10 to 13 feet in diameter, is composed of hewn blocks of hard stone, usually quartz porphyry, 6 to 8 inches thick, set on edge, the spaces between them being filled with sand or cement. Such a bottom lasts about 12 months, and it is surrounded by a rim of flat stones 6 to 8 inches thick, projecting to a height of 2 feet above the bottom. In the centre of the *arrastra* is a large pyramidal stone with a hole in its upper end. In the latter, fits the pivot of a vertical shaft with either 2 or 4 horizontal arms, supported at its upper end by a horizontal beam. Fastened by chains or leather thongs to each of these horizontal arms are the grinding stones (*voladoras*), one or sometimes two to each arm, so that when the latter revolve the *voladoras* are dragged over the floor of the *arrastra*. The stones are rectangular blocks of quartz porphyry weighing from 6 to 12 cwt., and they are fastened in such a way that their front lower edges are about 2 inches from the ground, the hinder end rubbing on the paved bed. These stones last from one to three months. The *arrastras* are worked by horses, mules, or by water or steam power.



FIGS. 426 and 427.

The older form of *arrastra* driven by mules is shown in Figs. 426 and 427 on a scale of $\frac{1}{120}$; *a* are the bottom stones and *b* the raised ones forming the rim, *c* the vertical shaft, resting on the stone *l* and supported by the horizontal beam *d*. To each of the four arms, two only of which are shown in the drawing, the stones *k* are fastened by chains, and the mules are yoked on to the long arm *x*, from one to six animals being employed, according to the size of the *arrastra*.

An *arrastra* driven by a horizontal water wheel is shown in Figs. 428 and 429, *a* being the wheel which surrounds the *arrastra*, connected to the vertical shaft of the same by means of the arms *z* and the connecting pieces *t*. Through the spout *b*, which has a slope of 8 inches in a length of 11½ to 15 feet, a stream of water is directed



FIGS. 428—429.

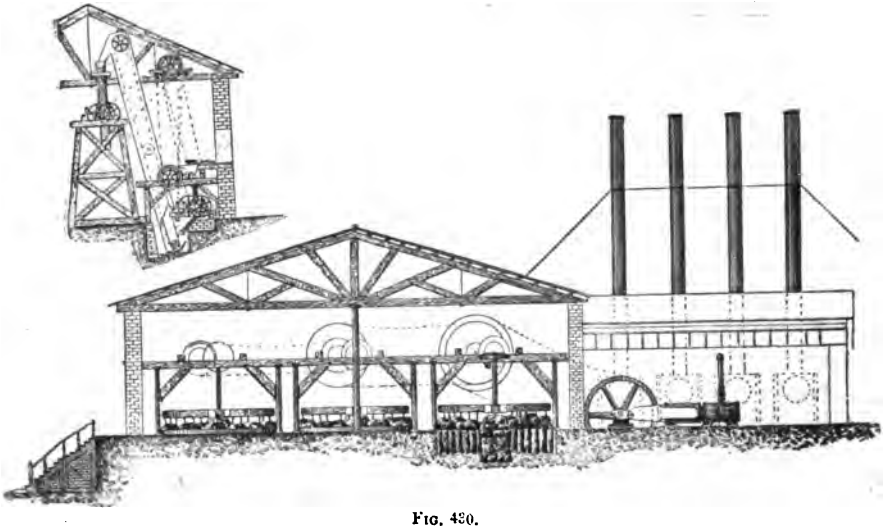


FIG. 430.

on to the buckets of the wheel. If the *arrastra* is 10 feet in diameter, it will occupy a space 23 feet in diameter, its water wheel being 20 feet in diameter and 2 feet broad. A mill 10 feet in diameter can grind 8 to 12 cwt. of soft ores in 24 hours, whilst 14 to 16 cwt. of hard ores can be finely ground in 3 days, but such a mill can of course only be used where a considerable water supply is available.

At Chihuahua, in Mexico, a similar water wheel works both the stamps and the *arrastra*. In some places overshot wheels, connected with the mill by wooden gearing, furnish the motive power.

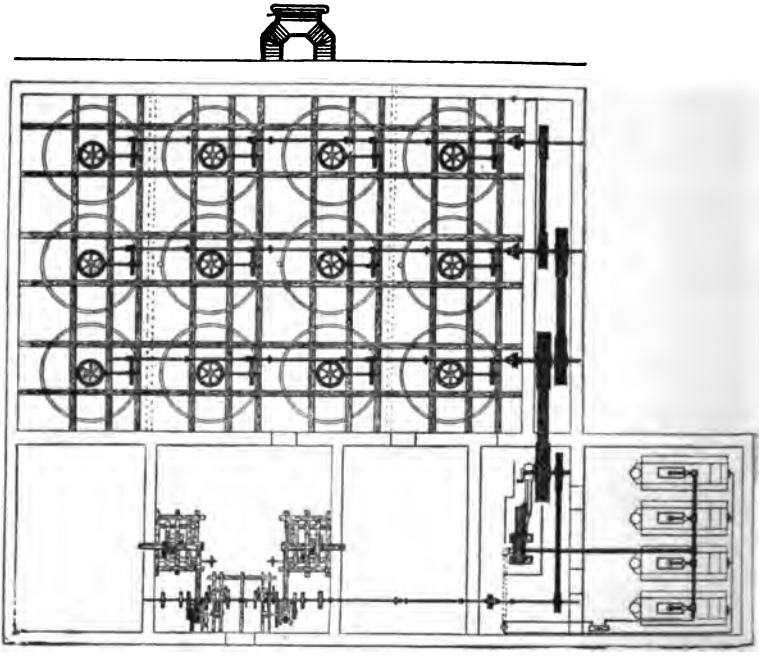


FIG. 431.

A set of steam-driven *arrastras* made by Fraser and Chalmers, Ltd., of Chicago, is illustrated in Figs. 430 and 431. The *arrastras* themselves are from 13 to 23 feet in diameter, and the granite grinding stones in them weigh 5 to 12 tons. Corliss engines are used for driving.

A similar plant has been erected at the works of the Edward Morrison Consolidated Mining Co. at Zacatecas in Mexico, the ores being first crushed in rock crushers, then passed through rolls, and lastly ground in the *arrastras*. The latter are 13 feet in diameter,

and each requires 6 horse-power, their capacity varying from 6 to 10 tons in the 24 hours, according to the nature of the ores.

In the *arrastras* the ore is crushed in presence of water, from 31 to 42 cubic feet of water being required for 8 to 12 cwt. of ore. The ore is introduced by degrees, sufficient water being added to each portion to convert the mass into a thin mud. The entire charge is ground with the mill stones making at first 6 revolutions per minute, increased as the ore gets finer, to 10 revolutions, until it feels slimy when rubbed between the fingers. The ground ore is then removed from the *arrastra* and transferred to the amalgamating floor or *patio*, With *arrastras* worked by mules, from 6 to 15 cwt. can be ground in 24 hours, depending upon the hardness of the ore and the size of the *arrastra*.

If native silver or gold is present, mercury is added during the grinding process in order to collect these metals, as has already been described under direct amalgamation.

In rare cases the ground ore is washed before being amalgamated, with the object of separating the horn silver from the sulphides, the former being treated by the Cazo process, and the latter going to the patio amalgamation process.

2. Amalgamation of the Ground Ore in the Patio

The ground ore from the *arrastras* is in the form of thin mud, and is termed *lama*. It is first put on the amalgamating floor or *patio*, in smaller heaps, so that it may dry to a certain extent, and then it is made up into the amalgamation heaps or *tortas*. The *patio* consists of a spacious courtyard paved with special care, so as to make it as impervious as possible to mercury. Cement and asphalt have been used for this purpose, and the floors have even been made of timbers carefully fitted into each other; but, as a rule, careful paving alone is depended on. The *patio* slopes slightly towards one side, so that any water draining from the heaps may flow away. In small *patios* the *tortas* are sometimes surrounded with a barrier of sand or with wooden planks to confine the contents of the heaps, which in larger works are spread on circular walled spaces known as *cajetes* or *lameros*.

After the water has drained away and evaporated, so as to leave the mass of the consistence of thick mud, which is the case after a few days, it is made up into the proper amalgamation heaps or *tortas* (*torta*, a cake).

As the ore mass is not yet very consistent, the *torta* has to be confined by pieces of timber arranged round it or by large stones, the

joints being made tight with clay or dung. The *torta* has now the shape of a large flat round cake, the thickness of the layer varying from 6 to 12 inches, and the diameter from 23 to 50 feet. From 50 to 100 or even 150 tons of ore are contained in each *torta*, the appearance of a *patio* with its several *tortas* being shown in Fig. 432.

Twenty-four hours, at the latest, after the *torta* has been made, the treatment with reagents is begun, salt being added first, then bodies containing copper sulphate and known as *magistral*, and then mercury, the mercury either being added with the *magistral*, or immediately after it.

If procurable, salt is added in the purest possible state, but in various places in Mexico, where the price of pure salt is too high, an impure salt, made by extracting the residues left after the evaporation of inland lakes, and known as *saltierra*, is used instead. Such salt contains from 70 to 90 per cent. of sodium chloride and 10 to 15 per cent. of sodium carbonate.



Fig. 432.

Either pure blue vitriol is used or the older *magistral*, produced in Mexico by roasting copper pyrites in double-hearthed reverberatory furnaces or *comalillos*, whereby some of the copper is converted into sulphate. The following analyses show how the *magistral* varies in composition according to the nature of the ore, and the care bestowed on it during the roasting operation:—

	Poor *Magistral*.	Best *Magistral*.
Copper sulphate	9·03	19·00
Copper oxide	5·0	5·5
Ferric sulphate	6·75	14·8
Ferric oxide	18·75	25·8
Insoluble matter	60·47	34·9

In default of sulphuretted ores of copper, copper sulphate can be made by roasting ores containing carbonate or oxide of copper with pyrites, or by treating such ores with ferric or aluminium sulphate or easily disintegrated pyrites. Thus, in Chili and Peru, the copper sulphate is made by treating a naturally occurring sulphate of iron

with copper oxide. Calcined pyrites has also been used instead of the copper salt, but the extraction by the iron sulphate thus obtained is very imperfect and does not amount to more than half of the silver in the ore. Owing to the comparatively small amount of copper sulphate in *magistral*, the latter has in many cases been recently replaced by pure copper sulphate.

The quantity of salt added to the *torta* varies from 2 to 5 per cent. of the weight of the ore, the larger the amount the better for the amalgamation, as the silver and cuprous chlorides, formed in the process, are soluble in salt solution. Ores with 0·09 to 0·1 per cent. of silver receive an addition of 4 per cent., ores with 0·13 to 0·23 per cent. of silver, 4½ per cent. of salt.

The salt is strewn over the surface of the *torta* as evenly as possible and then shovelled into the mass, after which the heap is trodden by mules and horses in order to ensure intimate admixture From 8 to 25 mules are used, a 60-ton *torta* requiring 16, and a 100-ton *torta* 25 mules.[1]

The condition of the ore mud during this *trituration* must be such that the animals' feet can tread through it to the paved floor and can also easily be withdrawn, whilst the holes left by their hoofs must only be effaced after the lapse of some seconds. The *torta* is trodden for some hours at intervals of several hours throughout the day, and whilst the mules are resting, the heap is turned over with shovels. The next morning the heap is again subjected to further treading and is further mixed with shovels, when the salt will be sufficiently mixed with the ore. This operation is termed *repaso*. As the treading is very exhausting for the animals, many attempts have been made to replace it by mechanical mixing, as, for instance, by employing weighted rollers fastened to horizontal arms connected to a vertical shaft. The shaft may be turned by mules walking round the edge of the *torta*, and by means of gearing the rollers can be made to pass over every portion of the heap, but such contrivances have proved uniformly unsuccessful.

After the mixing of the salt, the next operation is the *incorporation* of the *magistral* or copper sulphate, the mercury being rarely added until afterwards. The amount of *magistral* used depends upon its percentage of copper sulphate and upon the nature of the ores, being usually between ½ and 2 per cent. of the weight of the ore. If blue vitriol is used, 0·2 to 0·25 per cent. of the weight of the ore is added with ores carrying 0·09 to 0·19 per cent. of silver.

[1] Laur, "Métallurgie de l'Argent au Mexique, *Ann. des Mines*, séries 6, vol. xx., p. 65.

The *magistral* or copper sulphate is spread as evenly as possible over the surface of the mass and mixed in with wooden shovels, the mass being then subjected to a further treading or *repaso*. The *torta* becomes warm owing to the reaction between the copper sulphate and salt, and becomes darker and more porous.

In most works the mercury is added immediately after the incorporation of the *magistral*, that is, where it has not been added with the *magistral*. The method of allowing the *torta* to stand for some days after the *magistral* has been added, before adding the mercury, with a view of giving more time for the copper chloride to form silver chloride, has not proved a success and has been abandoned, the yield of silver being very much smaller than where the mercury is added immediately after the incorporation of the *magistral*. The reasons are that the native silver present is amalgamated by the mercury alone, and the more perfectly the longer it is in contact with it; that owing to the mutual reaction between the *magistral* and salt, considerable amounts of cupric and ferric chlorides are produced, which when in excess, convert the mercury into mercurous chloride, and that the chief reactions in the *torta* only begin after the addition of mercury. The real decomposition of the silver compounds should only take place therefore after the mercury has been added.

From 6 to 8 times the amount of silver present in the ore represents in general the quantity of mercury added, though at Zacatecas, according to Clement, the mercury added is only 3 times the weight of the silver present. At many works $\frac{2}{3}$ of the total amount of mercury is first added, at others $\frac{3}{4}$ of the amount, and at other works considerably less than $\frac{2}{3}$, the rest of the mercury being added as required.

The mercury is scattered over the surface of the *torta* in the form of exceedingly fine globules, the mercury being put in a bag of sail-cloth holding about 9 or 12 lbs., which is carried by a man walking over the heap, when the mercury finds its way through the cloth as a fine rain. Immediately after the addition of the mercury the mass is again trodden by mules, and mixed with shovels when the mules are resting. The mules for this operation are never more than 8 in number, yoked together in fours, and driven by a man standing in the centre of the *torta* in such a way that they are made to cover every part of the heap. A further addition of *magistral* or copper sulphate is made and trodden in, or sometimes a hot solution of copper sulphate after the treading in of the mercury, the amount to be added being decided by the amalgamation master. Samples are taken by the latter several times in the day and tested in order to ascertain

what additions should be made, and what the duration of the next treading or *repaso* should be. As a rule, the *torta* is trodden several times a day in order to expose fresh surfaces of the silver to the action of the mercury, as otherwise the silver becomes coated with a layer of silver amalgam which hinders the further action of the mercury.

The treatment of the *torta* lasts from 3 to 6 weeks, according to the character of the ore, the manner of working, the prevailing weather, and the skill of the amalgamation master, but in unfavourable circumstances it may last for some months. The amalgamation is considered to be finished when at least 75 per cent. of the silver contents of the *torta* have been extracted. In the ordinary course of working, the amalgamation proceeds more quickly in the first few days than at a later period; for instance, silver assays made on a *torta* at Guanaxuato in Mexico, showed that after 12 days the amalgam contained 92·79 per cent. of the silver obtained ultimately, after 25 days 97·55 per cent., after 28 days 99·1 per cent., and 100 per cent. at the end of 33 days.[1]

The assay samples from which the amalgamation master forms his estimates of the various reagents required by the *torta*, are usually taken three times a day from different portions of the heap by means of a horn spoon, about half a pound being taken for each sample. This is washed in a horn spoon or earthenware bowl (*platillo*) 7 inches in diameter, and $\frac{3}{4}$ of an inch deep. A rotary movement is imparted to the bowl in the washing process, the lighter portions of ore being washed away, the heavier portions forming concentric rings, according to their specific gravity, at the bottom of the bowl. In the centre is the mercury unaltered, then follows a ring of amalgam (*ceja*), then a ring of undecomposed black silver sulphide, then a ring of pyrites, and lastly one of *floured* mercury. If the mercury seems dull and of a lead-grey colour, the *torta* contains too much *magistral* or is said to be too hot (*caliente*), and there has been too much cupric or ferric chloride formed, leading to loss of mercury owing to the formation of calomel. In such cases the *torta* is either allowed to remain at rest for several days or else wood ashes, lime or precipitated cement copper are added. Wood ashes and lime precipitate carbonates or hydrates from the *magistral* or the chlorides present, whilst copper reduces cupric or ferric chloride to cuprous or ferrous chloride respectively. Zinc and iron act in a similar way to copper.

If the mercury, is very bright and quite unattacked, or possesses a tinge of yellow, the operation is proceeding too slowly, and the

[1] Laur, *op. cit.*

torta is said to be too cold (*frio*). The reactions are then hastened by further treading or by the addition of more salt and *magistral* and subsequent treading.

In normal working, the amalgam (*limadura de plata*) should be in the form of thin scales, which can easily be separated from the mercury which drains from it, and which can be pressed by the fingers into a dry mass (*pasilla*). If it can be completely divided by the fingers into little drops, the action has not proceeded far enough and the amalgam is too poor in silver, and if on the contrary it forms hard lumps which do not yield liquid mercury on pressing, it is too concentrated (*fuerte*). In this case, there is too little mercury in the *torta* and more must be added.

These appearances vary with different ores and in different localities, and are not always to be relied on. In certain cases, in spite of the favourable indications given by the amalgam, the process does not proceed properly in the *torta*, and in these cases in warm weather, additions of salt are usually required. The most reliable method of testing the progress of the operation is to determine by assay the amount of silver still remaining in the ore.

The operation is not only dependent upon the additions of the proper amount of the reagents, but is also dependent upon the temperature and the prevailing weather. A high temperature hastens the amalgamation and a low temperature retards it, the process ceasing entirely if the temperature falls to the freezing point. Falls of rain dilute the salt solutions in the *torta* and render further additions of *magistral* necessary.

In cold districts, heating the mass has been practised, the *torta*, after about half its silver has been amalgamated, being brought into a chamber with flues under the floor. In this room, (*estufa*), the *torta* is heated for three days and then taken and spread again on the *patio*, where the amalgamation is finished. The yield of silver is increased in this way, but there is such a considerable loss of mercury that the process has been abandoned.

When the amalgamation in the *torta* is finished, more mercury is added to it and trodden in with the mass, so as to render the amalgam more fluid and to collect it together. After this the *torta* is washed without delay in order to separate the mercury and amalgam from the remaining earthy portions of the ore.

If the *torta* is allowed to stand before washing, some loss of silver may take place, owing to the production of very finely-divided amalgam (*desecho*) arising from the action of copper sulphate.[1]

[1] Egleston, *Silver, Gold and Mercury*, i., p. 298.

The Chemical Reactions in the Torta

As already stated at the beginning of the chapter, the chemical reactions of the Patio process are not known with absolute certainty, and there is still a large field open for chemical research. Though a number of the reactions have been ascertained through the researches of Karsten, Boussingault,[1] Grützner,[2] Bowring, Uslar, Laur, Huntington and Rammelsberg,[3] there are still considerable differences in their views as to the manner and the degree in which these reactions proceed in the *torta*. Particularly are their views divided upon the questions as to whether the formation of silver chloride takes place to any great extent or not, whether cupric or cuprous chloride plays the chief part in its formation, and whether the copper oxychloride produced from the cuprous chloride plays an essential part in the decomposition of the ores.

The following reactions may be taken as having been clearly proved:—

1. Copper sulphate and sodium chloride mutually react in the *patio* forming cupric chloride and sodium sulphate, thus:—

$$CuSO_4 + 2NaCl = Na_2SO_4 + CuCl_2.$$

2. Cupric chloride is converted into cuprous chloride by the action of mercury or of native silver present in the ore, according to the equations:—

$$2CuCl_2 + 2Hg = Cu_2Cl_2 + Hg_2Cl_2,$$
$$CuCl_2 + 2Ag = 2AgCl + Cu_2Cl_2,$$

(Copper or cuprous sulphide present in the *torta* also converts cupric chloride into the cuprous salt, and cuprous chloride is formed as the result of the action of ferrous chloride upon cupric oxide, both of which bodies may be present. According to Rammelsberg's later researches the idea that cuprous chloride is formed by the action of silver sulphide on cupric chloride is erroneous, cupric sulphide only being formed according to the equation:—

$$Ag_2S + CuCl_2 = 2AgCl + CuS).$$

3. Silver sulphide is converted into silver chloride by the action of both cupric and cuprous chlorides.

Cupric chloride reacts with silver sulphide in this way:—

$$Ag_2S + CuCl_2 = 2AgCl + CuS.$$

[1] *Annal. Chim. Phys.*, 51, p. 337 (1834).

[2] Grützner, *Die Augustin'sche Silber extraction*, 1851.

[3] Percy-Rammelsberg, "Metallurgie des Silber und des Goldes," *Preuss. Minist.-Zeitschr.*, Bd. 29, s. 191.

Cuprous chloride dissolved in salt solution, reacts, according to the most recent of Rammelsberg's researches, upon silver sulphide in such a way that the products are silver chloride, cupric sulphide and metallic copper, according to the equation :—

$$Ag_2S + Cu_2Cl_2 = 2AgCl + CuS + Cu.$$

Rammelsberg's researches agree with those of Boussingault with this difference, that the latter considers that cuprous sulphide is formed as follows :—

$$Ag_2S + Cu_2Cl_2 = 2AgCl + Cu_2S.$$

According to Laur's researches, the reaction between cuprous chloride and silver sulphide in presence of mercury gives rise to no silver chloride, the silver being liberated in the metallic state with the simultaneous formation of cupric sulphide and chloride, in this way :—

$$Ag_2S + Cu_2Cl_2,NaCl = CuS + 2Ag + CuCl_2,NaCl.$$

4. Silver sulphide, present in mixed sulphides such as sulph-antimonides or sulph-arsenides of silver, is decomposed by cupric chloride with the formation of silver chloride, or by cuprous chloride with production of silver chloride, or a mixture of silver chloride and metallic silver. According to Rammelsberg, cupric chloride acts upon proustite in this manner :—

$$4Ag_3AsS_3 + 12CuCl_2 = 8AgCl + 2Ag_2S + 2CuS + 2As_2S_3 + 2S,$$

and upon pyrargyrite in this way :—

$$2Ag_3SbS_3 + 3CuCl_2 = 6AgCl + 3CuS + Sb_2S_3.$$

The action of cuprous chloride upon pyrargyrite, according to the same authority, is represented as follows :—

$$2Ag_3SbS_3 + Cu_2Cl_2 = 2AgCl + Ag_2S + 2Ag + 2CuS + Sb_2S_3.$$

5. Silver sulphide, either alone or present in combination with other metallic sulphides, is decomposed by mercury into metallic silver or amalgam, and mercuric sulphide is formed according to the equation :—

$$Ag_2S + 2Hg = Ag_2Hg + HgS.$$

6. Silver chloride is reduced to metal by the action of mercury with the formation of mercurous chloride thus :—

$$2AgCl + 2Hg = Hg_2Cl_2 + 2Ag.$$

7. Silver present in the native state in the ores is only superficially converted into silver chloride, being for the greater part taken up directly by the mercury.

According to Rammelsberg, and also to Karsten and Sonneschmidt, by the action of cupric chloride arising from mutual reaction between sodium chloride and copper sulphate, the greater part of the sulphide of silver existing free, or combined with other sulphides in the ores, and a small portion of native silver, are converted into silver chloride.

Cuprous chloride, formed by the action of mercury and silver upon cupric chloride, converts only a small percentage of silver sulphide into chloride, as the salt is very soon converted into oxychloride by the oxygen of the air, in which state it is not capable of any further action. The chloride of silver is reduced to metal by the mercury present, with formation of mercurous chloride, and the liberated silver unites with the excess of mercury, forming amalgam.

A considerable portion of the silver sulphide in the ores is decomposed by the mercury, silver separating and mercuric sulphide being produced, the liberated silver, together with that present in the ores in the fresh state, amalgamating with the mercury.

That the whole of the silver is not liberated by the action of mercury on silver chloride is evident from the amount of mercury used in the process; 400 parts of mercury would in such a case be required for the production of 216 parts of silver, whereas in practice in the Patio process, the mercury lost, including the considerable mechanical loss, does not amount to more than $1\frac{1}{2}$ times the weight of silver obtained.

According to the researches of Boussingault, Bowring, Uslar, Grützner and Laur, cuprous chloride plays the chief part in the process, and not the cupric salt.

Boussingault assumes that silver sulphide present either as such or in combination with other sulphides, is first decomposed by cuprous chloride with the production of silver chloride, and that the latter is then decomposed by the mercury present. The other metallurgists deny that silver chloride is formed in this way, and hold that silver is separated directly in the metallic state by means of cuprous chloride, in presence of oxygen or of metallic silver.

Cuprous chloride is produced, as mentioned before, by the action of mercury, native silver, copper, zinc, or copper or zinc amalgams upon cupric chloride, and is also formed by the action of cupric chloride upon cuprous sulphide present in the ores, and by a mutual reaction between cupric oxide and ferrous chloride, the latter salt being produced by the reaction between ferrous sulphate in the *magistral* and the added salt.

According to Boussingault's views the reactions in the *torta* are

as follows: By the action of salt on the *magistral*, cupric chloride is produced, which body acts, however, only to a very slight extent upon silver sulphide, because it is reduced by the mercury to cuprous chloride. The latter salt dissolves in the common salt solution present, penetrates through the mass of ore, and converts the silver of the simple and compound sulphides into silver chloride, copper sulphide being produced, or, according to Rammelsberg, cupric sulphide and metallic copper. The silver chloride formed, dissolves in the salt solution and is decomposed by mercury, silver separating in the metallic state and alloying with the mercury, and calomel being produced at the same time.

Bowring, Uslar and Grützner assume that cuprous chloride produced in the manner previously mentioned is the principal agent in the process, and that silver chloride is not produced to any extent, the cuprous chloride in presence of oxygen liberating silver from the sulphide in the metallic state.

According to the views of the two first-named, the cuprous chloride formed is converted into oxychloride by atmospheric oxygen, according to the equation:—

$$Cu_2Cl_2 + O = CuCl_2CuO.$$

This oxychloride liberates silver from silver sulphide with formation of cuprous chloride. The reactions further given show a very imperfect knowledge of chemical changes, as the sulphur of the silver sulphide is assumed to be oxidised to sulphur dioxide by the oxygen of the copper oxychloride, and this sulphur dioxide, together with more oxygen and a further quantity of oxychloride is supposed to liberate chlorine from common salt, the cuprous chloride being oxidised to cupric chloride by the chlorine set free.

According to Stölzel[1] the process may be represented as follows, eliminating the impossible reactions:—

$$3(CuCl_2,CuO) + Ag_2S = 3Cu_2Cl_2 + SO_3 + 2Ag,$$

cuprous chloride being produced in addition to sulphuric acid, and being converted again into oxychloride by the oxygen of the air.

According to Grützner,[2] copper oxychloride is not produced at all, but cuprous chloride in presence of atmospheric oxygen liberates silver from silver sulphide with the formation of cuprous sulphide, cupric chloride and sulphuric acid, according to the equation:—

$$2Ag_2S + 2Cu_2Cl_2 + 3O + H_2O = 4Ag + Cu_2S + 2CuCl_2 + H_2SO_4.$$

[1] *Metallurgie*, "Silber," p. 1235.

[2] *Die Augustin'sche Silber Extraction*, 1851.

According to Laur, cuprous chloride liberates silver from the sulphide without the action of oxygen, but in presence of mercury and common salt, producing cupric sulphide and calomel, Stölzel's equation for this reaction being :—

$$2Ag_2S + Cu_2Cl_2 + 2Hg = 4Ag + 2CuS + Hg_2Cl_2.$$

This view of Laur's is based upon his own researches, and upon the fact that the chief reaction in the *torta* only begins after the mercury has been added and trodden in. Laur has shown that native silver sulphide brought into contact with a solution of copper sulphate and common salt in presence of copper and mercury, is in a short time completely converted into free silver, cupric sulphide or cupric sulphide and calomel being formed. This rapid decomposition of the sulphide does not take place in the absence of copper or mercury.

The cupric sulphide resulting from the decomposition of the silver sulphide can be converted into cupric sulphate by the action of air, and this in turn is converted into chloride by the action of common salt. The mercury then reacts with this cupric chloride, converting it into the cuprous salt, copper oxychloride not being formed, as the cuprous chloride as fast as it is produced, acts upon the silver sulphide.

From these views upon the reactions taking place in the *torta* it will be gathered—(1) That the extent to which cuprous and cupric chlorides take part in the decomposition of the silver ores is still not established. (2) That the question to what extent the silver present as a simple sulphide or in combination with other sulphides, is converted into silver chloride, or to what extent it is liberated as metallic silver without previous formation of chloride, is up to the present unanswered. (3) That there is no explanation of the mode of action of copper oxychloride upon the metallic sulphides present in the *torta*.

The author holds the following view of the reactions which go on in the *torta*. Cupric chloride is first formed by the reaction between copper sulphate and sodium chloride. As this salt only decomposes silver sulphide very slowly, the principal part in the decomposition of the silver compounds must be assigned to cuprous chloride, and this is in accord with the fact that the main reaction in the *torta* does not begin until the mercury has been incorporated (that is, until the cupric chloride has been reduced to cuprous), and that cuprous chloride, as in the Kröhnke process, is known to rapidly decompose the silver compounds present. As, however, cuprous chloride exposed to the air is rapidly converted into oxychloride, it must act upon the silver ore as fast as it is formed. It seems probable, on the

basis of Laur's experiments and observations, that in contact with mercury and silver sulphide, metallic silver, copper chloride and copper sulphide are produced, though the reaction, by which, according to Rammelsberg and Boussingault, a portion of the silver is converted into chloride, according to the equation :—

$$Ag_2S + Cu_2Cl_2 = 2AgCl + CuS + Cu,$$

is not absolutely excluded.

That silver chloride may be produced as well as free silver, follows from Rammelsberg's observations on the action of cuprous chloride upon pyrargyrite, the reaction being represented as follows :—

$$2Ag_3SbS_3 + Cu_2Cl_2 = 2AgCl + Ag_2S + 2Ag + 2CuS + Sb_2S_3.$$

A portion of the silver sulphide is reduced by metallic mercury; native silver present in the ore is partially converted into silver chloride by cupric chloride, cuprous chloride being produced, and partly taken up directly by the mercury. The silver chloride produced is decomposed by mercury, and the silver separated is amalgamated by the excess of mercury.

Exact knowledge of the reactions in the *torta*, especially as to the extent to which the various reactions take place, and the part played by copper oxychloride, can only be arrived at by further research.

3. The Separation of the Amalgam from the Amalgamated Ore

The separation of the mercury and the amalgam from the amalgamated ore is effected by washing with water in vats or tanks. Vats are chiefly in use, and they are provided with agitators worked by mules. They are made of wood or masonry, and are placed either in the floor of the *patio* or above it.

The *torta* is agitated for some hours with water, the heavier portions allowed to settle, and the supernatant liquid with the lighter portions suspended in it, is drawn off through openings some distance from the bottom, and run into a second and sometimes a third and fourth vat.

The construction of an old form of washing vat (*tina*) with agitators driven by mules, and sunk in the floor is shown in Fig. 433.[1] *A* is the vat made of masonry, the bottom *z* being constructed of a single block of porphyry. The stirrers *r*, *r* are fastened to the vertical shaft *B*, and are worked by a driving wheel *y* on the main shaft *w* gearing into a pinion wheel *q*; *q'* is the wheel of another agitator working in

[1] Percy, *Silver and Gold*, p. 622.

a similar vat lying beside the other one, but not shown in the figure. The mules are yoked to the arms (*i*, *i*), and walk round on the floor *m*. In such a vat 46 cwt. are washed per hour, the amalgam collecting at the bottom of the vat and being afterwards scooped out of it.

At the Hacienda de Rocha, Guanaxuato, the plant for washing consists of 4 vats,[1] the greater part of the amalgam settling in the first one, and the slimes passing consecutively into the second, third and fourth vats, in the last of which almost all the suspended amalgam is collected. The slimes flowing from the last vat are deposited in a special reservoir, and are afterwards washed, yielding slimes rich in pyrites and carrying up to 3 per cent. of silver. About 600

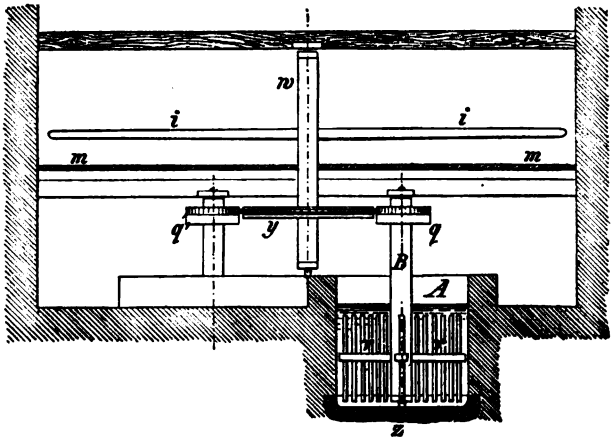


FIG. 433.

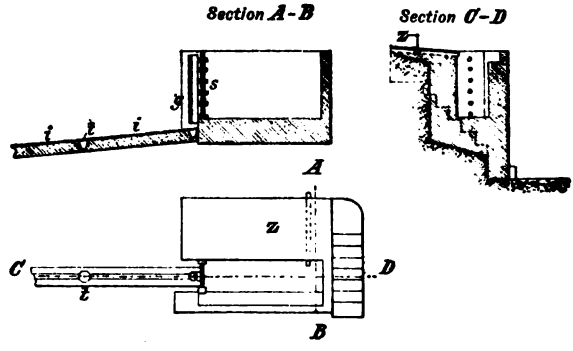
quintals of ore (1 quintal = 100 lbs.) are washed in 24 hours. The amalgam remaining in the vats is still mixed with heavy portions of the ore, and is washed in wooden bowls (*bateas*) in a large vat partially filled with water, the operator working the *batea* with a peculiar shaking movement. The washed amalgam is then placed in a smooth stone trough, mercury is added to render it more liquid, and any fine particles of ore collecting on the surface are wiped off with flannel. The amalgam is finally repeatedly stirred up with water until it shows a pure reflecting surface.

An arrangement of washing tank, where the slimes are washed by treading with the feet, is shown in Figs. 434, 435, and 436. This tank or *lavadero* is 6 feet 6 inches long, 20 inches wide, and 3 feet deep, and

[1] Percy, *Silver and Gold*, p. 623.

is of masonry lined with cement. The front side is of wood and has 6 perforations *s*, *s*, each 2 inches in diameter, closed by wooden plugs. A vertical spout *g* is placed in front of these holes, through which the slime runs into a sloping trough *i*. At the bottom of this trough are several depressions *t* filled with mercury with the object of collecting any mercury or amalgam flowing down the trough.

This tank is half filled with water, and two workmen stand in it, whilst a third gradually adds the slime from the platform *z*, the top plug being withdrawn. The workmen in the vat keep the slime in constant motion with their feet, the heavier portions settling to the bottom, whilst the lighter parts flow off through the top plug hole, water being added constantly to make up for that flowing away with the slime. The slime flows away along the spout *i*, over the mercury catchers *t*, into a slime pit. From time to time a portion of the



FIGS. 434—436.

liquid is allowed to flow from the next lower hole. The amalgam is only removed after the whole of the *torta* has been washed, the flow of water being stopped, and the plugs withdrawn one by one, commencing with the top one.

The portions of the *torta* separated from the amalgam still contain some portions of ore of which the silver content has escaped amalgamation. It is therefore washed, usually in a very simple form of apparatus known as the *planilla*, the arrangement of which is illustrated in Figs. 437 and 438. The *planilla* consists of a sloping bed of marl or fine slimes *H*, rammed into a wooden or masonry framework and having a water reservoir at the bottom. The marl bed is 11 feet 6 inches long and 7 feet 6 inches broad. The ore slime is made into a heap at the top of the bed *k*, and water is thrown on to it from a horn spoon holding about 9 ounces, the lighter portions being carried

away and the heavier part remaining behind. After a time the lighter portions, which will have collected in a layer extending to a distance of about 3 feet upwards from the reservoir, are removed, and the heavier portion lying further away from the reservoir is collected and again made into a heap at the head of the slope and the whole operation repeated. The product at last consists of black argentiferous sulphides called *polvillo*. This is washed in wooden bowls having the form of an inverted truncated cone 2 feet in diameter and 16 inches deep, in which the mass is stirred up with water, allowed to settle, and the water poured off. The residue consists of three layers, the upper one, consisting mainly of sand, which is thrown away; below this is a layer known as *colas*, consisting chiefly of poor sulphides, which



FIG. 437.

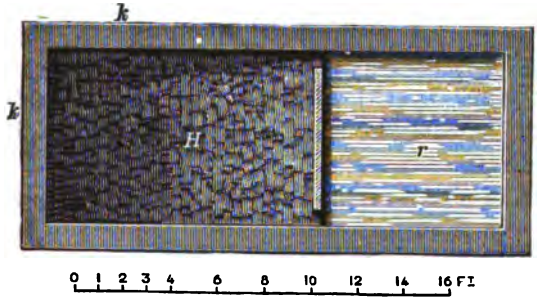


FIG. 438.

is roasted and added to a fresh *torta*, and the lowest layer consists of sulphides rich in silver with a small amount of amalgam. These sulphides are exported to Europe, or if they contain galena are smelted to obtain a silver-lead alloy. Cupriferous pyrites containing gold and silver are roasted and used as *magistral*.

At some works the slimes from the *planillas* are again washed on round buddles, and in this way another slime containing 0·2 per cent. of silver is obtained. Recently, at some Mexican works, the amalgamation residues have been submitted to a chloridising roasting, and the silver chloride produced dissolved out by calcium or sodium thiosulphate and then precipitated from this solution as sulphide by an addition of sodium or calcium sulphide.

4. The Treatment of the Silver Amalgam

The amalgam is put into a conical bag of sail-cloth (*manga*) suspended by an iron ring, a reservoir being placed below to catch the mercury draining away. After it has stood in this for some hours it is ready for heating in retorts. Formerly in most works it was rammed into iron moulds and withdrawn in the form of a circular cake (*bollo*), which was distilled in the bell form of apparatus. More recently it has been usual to press it into iron mercury bottles with the bottoms removed, and to distil it from these, a process to be subsequently considered.

The losses of mercury in the Patio process are partly chemical and partly mechanical. The chemical losses depend chiefly upon the nature and composition of the ore, and are the smaller the more silver is present in the native state. The entire loss, including the comparatively small loss in retorting, has been found to vary at different works from 87 to 400 per cent. of the silver produced, and on an average it may be reckoned that for every 1 part of silver obtained 1½ parts of mercury are lost. For instance, according to Laur, the loss for every 1 part of silver at the Quebradillas and La Granja mines at Zacatecas was 1·43 of mercury, at Guanaxuato 1·62, and according to Silliman, at the Hacienda Nueva at Fresnillo 1·65, and, according to Stetefeldt, at the Hacienda Sauceda at Zacatecas 1·62 parts of mercury.

The yield of silver varies in favourable circumstances from 75 to 80 per cent. of the assay content of the ore. With ores containing zinc blende it is about 70 per cent., whilst ores containing arsenical and antimonial sulphides may yield only 60 per cent.

The results obtained at the largest works in Mexico, the Hacienda Nueva, near Fresnillo, in the State of Zacatecas, may be quoted as illustrating the Patio process.[1] There are 12 stamp mills, 314 *arrastras*, accommodation for 1,500 mules, and a *patio* for 64 *tortas*, each 41½ feet in diameter, 900 tons of ore being worked weekly. From 1853 to 1862, 452,264 tons of ore were worked, yielding 1,096,281 marks of silver (1 mark = 8 oz. Troy), equal in value to 9,825,598 dollars. The salt used amounted to 6 per cent., the *magistral* to 1·75 per cent. of the weight of the ore, the loss of mercury being 1·65 times the weight of the silver obtained, the average loss of silver being 19·48 per cent., equal to a yield of 80·52 per cent.

In addition to the works in Mexico the Patio process is also in

[1] *Engineering and Mining Journal*, 1883, p. 394.

limited use in Peru, Chili, and Bolivia, but in most places it is being superseded by other processes (Cazo, Kröhnke, Francke, or smelting processes).

The Washoe Process of Pan Amalgamation

In this process the ore is first crushed in rock breakers, wet-stamped to powder and then transferred to cylindrical or slightly conical iron pans provided with an arrangement for stirring or rubbing the ore, the so-called *muller*. Here it is brought into intimate contact with mercury, copper sulphate and salt, together with warm water, and by this means the silver present in the ore, either native or as sulphide or chloride, is converted into silver amalgam. Arsenical and antimonial sulphide ores are not well adapted for the process, and may only be present in small amounts.

The amalgam obtained is washed in a special apparatus or settler in order to separate it from the residue, and is then filtered, pressed or squeezed, and distilled.

The stamped ore is put into the pans with sufficient water to convert it into a thin mud, and it is first rubbed there to the finest powder, and then heated by steam and submitted to the action of the necessary reagents with constant agitation. The chief reagents are metallic iron and mercury, and to a less extent copper sulphate and common salt. The iron is partly derived from the wear of the stamp mill and is partly supplied by the material of the pan and muller.

The mercury in presence of iron liberates silver from silver sulphide, and silver chloride is decomposed by the same reagents, forming metallic silver and calomel, which latter is reduced again to mercury by metallic iron. The liberated silver, as well as any free silver in the ore, is then amalgamated by the mercury.

To a less extent, reactions in which copper sulphate and common salt take part also occur, cupric chloride being produced and reduced to cuprous chloride by metallic iron and this then acts on silver sulphide and particularly upon sulpharsenides and sulphantimonides of silver as in the Kröhnke or Patio processes.

The ores are powdered by wet stamping, the process being thence also called the wet process of pan amalgamation, in distinction to dry pan amalgamation, in which the ores are crushed by dry stamping, and, owing to their refractory nature, must be submitted to a chloridising roasting previous to the amalgamating operation. The name "Washoe process" is derived from the district of Washoe in Nevada, where the process was first introduced in 1861. In 1859 a party of pros-

pectors looking for gold found the famous Comstock lode called after one of their number; this lode was 4·1 miles long and 65 to 650 feet wide, and for a long time was one of the most important sources of silver in the world. The ores of this lode consisted mainly of silver sulphide with native silver and gold, and two methods of working them were introduced. The richer ores, containing considerable quantities of pyrites, galena and blende, were submitted to a chloridising roasting, followed by amalgamation in barrels like those formerly in use at Freiberg. The other ores were amalgamated in pans without any preliminary roasting. The first method was subsequently abandoned and the latter alone used.

The Washoe process has gradually, since its introduction into the Washoe district for the working of the Comstock ores, followed by its employment in other districts in the States (Montana, Colorado), attained to a high degree of perfection.

The chief works in the Washoe district are the Consolidated Virginia Mill, and the California Mill, Virginia City. Ores for this process may not contain large quantities of sulph-arsenical and sulph-antimonial compounds of silver, nor large amounts of galena or blende; small amounts of these bodies are, however, decomposed by the cuprous chloride formed from the reagents added.

The ores of the Comstock lode contain native gold and silver, silver glance, polybasite, stephanite, proustite and pyrargyrite, also quartz, galena, zinc blende, iron and copper pyrites, oxides of iron and manganese, carbonates and sulphates of lime, magnesia, copper and lead. The silver content varies from 0·05 to 2·786 per cent., and the gold from 0·001 to 0·57 per cent.

The process is worked in the following way. The ores are first broken in rock breakers, and then pulverised with water by stamps. The pulp flows through a series of tanks, in which the greater part of the fine ore settles. The liquid flowing away, carrying still 2 to 10 per cent. of the original ore, is generally collected in large slime reservoirs where the slimes settle, and are treated with the rest of the ore. The crushed ore is taken out of the tanks and charged into the pans where it is first rubbed to fine powder, and then amalgamated with mercury and the reagents.

After the amalgamation is finished, the pulp is thinned with water and run off into settlers provided with agitators, where the amalgam which has not already been separated in the pans is washed free from the ore residue. At some works, the residue is still further washed in agitators to separate the last traces of amalgam and unaltered ore.

The residues from the settlers or agitators are known as tailings, and these are concentrated in order to obtain the heavy unaltered ore present in them. They are either run over broad, slightly sloping and very long tables, or through long troughs provided at short intervals with transverse grooves, or else worked by special dressing plant.

The amalgam is first freed from the excess of mercury contained in it by filtration through conical canvas bags, and is then distilled in horizontal iron retorts.

The impure solid amalgam which collects in the pans and the hard amalgam from the pans and settlers, is put into smaller cylindrical, iron, *clean-up* pans, and there agitated with water and additional mercury for several hours until quite clean and perfectly liquid, and it is then treated in the same way as the rest of the amalgam.

The plant required in the Washoe process is usually so arranged that the materials pass by gravity from one apparatus to the next succeeding, so that none of it needs to be lifted back again.

The various operations which will now be considered in detail are:—

1. The crushing of the ores.
2. The pan treatment of the ores.
3. The separation of the amalgam from the amalgamated ores.
4. The working up of the amalgam.
5. The treatment of the residues from the amalgamation.

1. The Crushing of the Ores

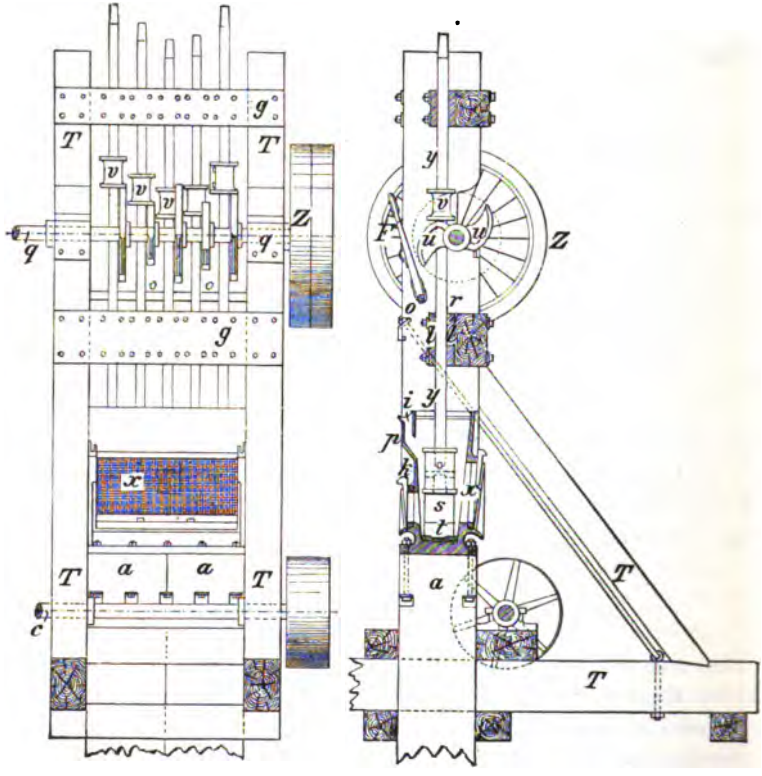
The ores as they come from the mine are run over a *grizzly*, and the finer portions taken direct to the stamp mill, whilst the large pieces are put through a stone-breaker. Blake's stone-breakers are usually used, or more rarely Dodge's, one Blake crusher serving for a mill of 60 stamps.

The stamp mills used in the Washoe process were devised in California, and are known as Californian stamps.

The stamp stems are round turned wrought-iron bars, which rotate during the process of stamping, shod with shoes of hard white iron or recently of steel, working upon dies of the same material. These dies are placed in a mortar of cast iron, cast in one piece. The screens of perforated iron or sheet steel through which the powdered material finds its exit, are placed either on one, or more rarely on both of the longer sides of the mortar. A battery consists

usually of 5 stamps, and the stems work in wooden guides at the top and middle of the stamp frame. The ore is usually fed in automatically by an arrangement with a shaking movement worked from the stamps themselves.

The arrangement of a battery of 5 stamps is shown in Figs. 439 and 440; *a* is the foundation of stout timbers, *p* the mortar box of cast iron in which are placed the dies *t*, and *i* is the feed



FIGS. 439 and 440.

shoot. Sieves *x* on both of the longer sides of the mortar allow of the discharge of the stamped material; the sieves are kept in place by wedges *k*. The stamp stems *y* work in wood journals *l*, and the stems carry at their lower end cylindrical pieces of iron or heads to which the shoes *s* are fastened; *u*, *u* are the cams working against tappets *v* keyed on the stamp stems. *F* is a *finger* or prop hinged at one end on the axle *o*, and so arranged that the other end will, by catching underneath the tappet *v*, support the stamp out of the reach

of the action of the cam when repairs are necessary. The shaft q driven by the pulley Z off the shaft c drives the cams; T, T are the uprights of the framework bound together by the cross pieces g g, which also carry the wooden guides for the stamp stems. A perspective view of a stamp battery for the Washoe process is given in Fig. 441.

With regard to the details of the chief parts of a battery, the foundation or mortar block consists of upright balks of timber fastened together with iron bolts. The height of these varies according to the nature of the soil, and the height at which the mortar is to be fixed, from 6 to 12 feet, and they are about 30 inches square, the

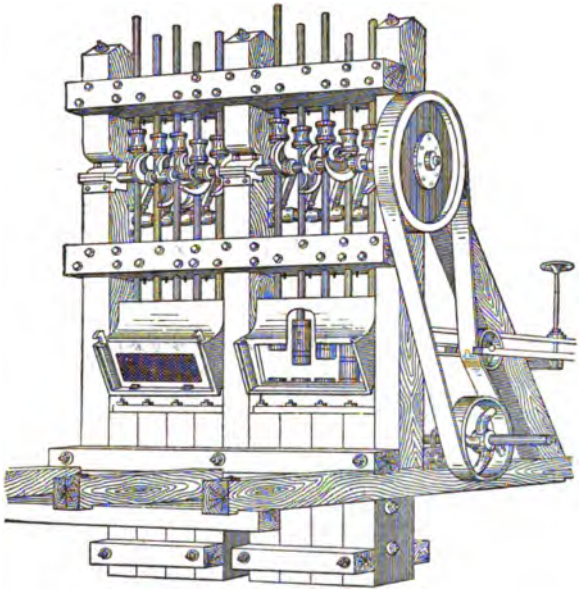


FIG. 441.

mortar blocks in use at the Consolidated Virginia Mine consisting of logs nearly 12 feet long and 30 inches square.

The mortar, which is bolted to the block, is made entirely of cast iron and has a length and height of from 4 to 5 feet, and an internal width at the bottom of 12 inches. The feed slot through which the ore is charged in is 3 to 4 inches wide and nearly as long as the mortar itself. If the mortar discharges on one side only the exit is placed on the opposite side to the feed slot, but where there is a double discharge, which increases the capacity of the mill, the feed slot is placed above the discharge at the back of the mortar.

The screen openings are nearly as long as the mortar, and possess a height of from 12 to 18 inches; they are closed by screens set in wooden frames kept in place by wrought-iron wedges. A mortar with double discharge is shown in cross section in Fig. 442, *r* being the wooden screen frame with the inclined screens, *k* the wedges for holding the frames in position, and *e* the feed slot.

For the Washoe process, screens of perforated sheet iron are to be preferred to those of wire gauze on account of their greater durability; the width of the holes varies from 0·0039 to 0·0236 inch.

Below each stamp a cylindrical die of hard, tough, white iron (*i*, Fig. 442) is placed in the mortar, and the dies are cast with a flat

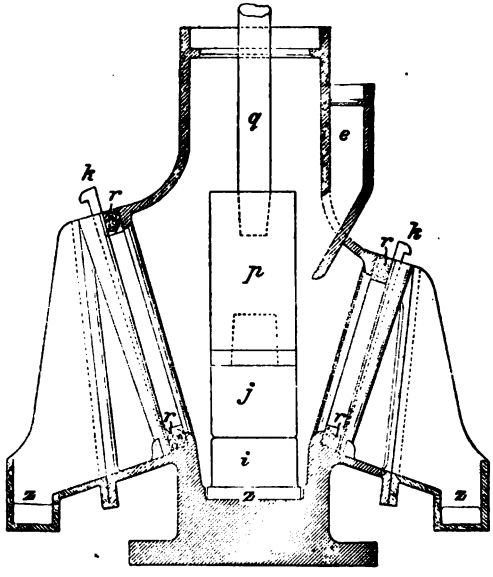


FIG. 442.

square base (*z*, Fig. 442), with bevelled-off corners. The die is 4 to 6 inches high, including the foot plate, and is of the same diameter as the shoe of the stamp (8 to 10 inches).

The shaft of the stamp consists of a round bar of turned wrought-iron, from 3 to 4¾ inches in diameter, and 10 to 12 feet long, and fastened to its lower end is a head or boss of tough cast iron, of 8 to 10 inches diameter, and 15 to 20 inches high. The details of this are shown in Figs. 443 and 444, the head having a slightly conical hole to receive the stamp stem at the top and another conical hole below to receive the shoe. In the older mills a stout wrought-iron hoop *g* was shrunk on to each end of the boss.

The shoe (Fig. 445) is of white iron or steel, having a conical shank *u* at the top to fit into the corresponding conical hole in the boss. The cylindrical portion varies from 8 to 12 inches in

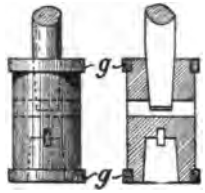


FIG. 443.


FIG. 444.



FIG. 445.

diameter and from 5 to 6 inches in height, and as soon as the height is reduced to 1 inch by wear it is replaced by a fresh one. When new the shoes weigh from 100 to 180 lbs.

The shoes are fixed in the heads by wooden slips fastened round the conical part with string, so that the cone can be driven into the conical hole of the head. In wet stamping, the wood becomes swollen and holds the shoe firmly on the head.

The tappets (*a*, Figs. 446 and 447) are cylinders of cast iron with holes bored through to fit on the stem to which they are fastened



FIG. 446.

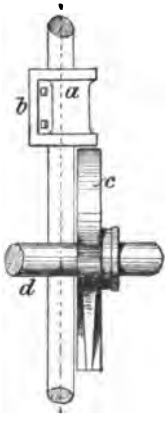


FIG. 447.

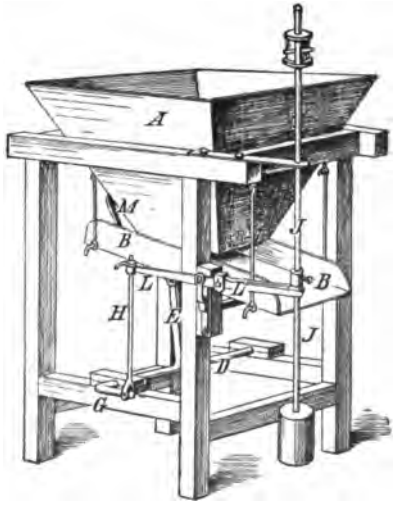


FIG. 448.

by keys. The cams (*c*, Figs. 446 and 447) have two arms and are made of tough cast iron (more recently of steel), and they not only lift the stem of the stamp, but impart to it a rotary motion at the same time.

The ore is charged into the mortar by a self-acting arrangement, one of the most generally used forms being shown in Fig. 448, and known as Tulloch's ore feeder. It consists of a shaking tray *B* placed below the ore hopper *A*. This tray is connected with the rocking shaft *D*, by an arm *E*; the shaft receives its motion from the rod *J*, with which it is connected by the two-armed lever, *L*, *L*, and the arm *H*. The rod *J* receives its motion from the tappet of the centre stamp of the battery, which comes in contact with the top end of the rod, a hole being bored through the lower guide block for this purpose. After each shake, the tray is brought back to its original position by a strong steel spring *M*. The extent of the movement imparted to the tray is varied according to the amount of ore lying in the mortar. If the dies are deeply covered with ore, the stamp does not fall through its full height, and the shake imparted to the tray is feebler and less ore is delivered. If, however, there is little ore in the mortar, the height of the fall is greater, and the tray receives a greater shake, delivering more ore in consequence.

The entire weight of a stamp varies between 7 and 8 cwt., the number of blows per minute being between 70 and 80, or even up to 100, the height of the fall varying from 7 to 10 inches. The capacity of a stamp is from 1 to 5 tons of ore in 24 hours according to the hardness of the ore, the quartzose ore of the Comstock lode being crushed at the rate of 2 to 3 tons in 24 hours.

The consumption of water is about 72 gallons per stamp per hour. The crushed pulp is led into a trough leading to a reservoir where the solid portions are allowed to settle. The troughs are 6 to 8 inches deep. From the reservoir the liquid runs through a slime pit and the settled liquid is usually allowed to run to waste. The tanks are so arranged that they can be cleaned out without interrupting the work, the pulp being in the meantime run into other tanks. At the Consolidated Virgina Mill, Virginia City, Nevada, working on the Comstock lode, the reservoirs, of which there are 42, are each 9 feet long, 5 feet broad, and 3 feet deep, and after each reservoir there is a slime pit of the same dimensions. The ore is taken out from the tanks with buckets fastened on handles and is thus charged into the pans.

2. The Treatment of the Powdered Ore in the Pans

The pans are vessels provided with agitators or mullers, and having the shape of short vertical cylinders or truncated cones. They are usually constructed of cast iron, but in many cases the sides are

of wood. Formerly, in order to save power, the bottoms of the pans were made conical, but at present they are mostly flat. The pans are from 4 feet to 5 feet 6 inches in diameter and 2 feet to 2 feet 6 inches deep.

The agitators, mullers or grinders serve the purpose of converting the ore into fine powder and of bringing it into intimate contact with the mercury and reagents added.

The simplest form of muller consists of a cast-iron cone, with a series of openings in the upper portion and provided on its lower surface with pieces of cast iron 2 to 2¾ inches thick, and weighing 5 to 8 cwt., known as shoes, and constituting the upper grinding surface. There must be at least six of these shoes.

The muller is attached to a vertical shaft in the centre of the pan, and can be raised or lowered by means of a screw.

The lower grinding surface is formed of iron plates placed above the true bottom of the pan, and consists generally of a series of separate blocks or dies of iron, with radial grooves between them. The action of the muller, which makes from 60 to 90 revolutions per minute, is to divide up the mercury on the bottom of the pan and to bring the small globules into intimate contact with the material of the ore pulp. Currents are set up owing to the shape of the shoes and the openings in the conical part of the muller, the ore pulp being thrown up against the pan sides, whilst the mercury sinks to the bottom. The ore pulp which has risen up the sides then sinks to the bottom down the central portion, again finds its way under the muller, and is then ground afresh between the shoes and dies and again brought in contact with the mercury, and so the process is repeated. In order to prevent the pulp from being carried to too great a height up the pan, wings are attached at intervals to the pan sides.

The reactions in the pan proceed most favourably when the temperature of the contents is raised to the boiling point of water, and for this purpose the pan is heated by means of steam. This is effected either by providing the pan with a false bottom and introducing steam into the intermediate space, or else by passing steam directly into the pan, or both methods may be used at once. The most usual plan is simply to lead steam directly through the pan contents, the steam for this purpose being taken direct from the boiler, as exhaust steam from the engines would be contaminated with oil or grease, which would hinder the amalgamation. Exhaust steam may, of course, be used for heating the double bottom. The pans are furnished with iron or wooden covers. From time to time

pans with slightly different arrangements have been introduced without, however, altering the essential principles of their construction. The pans differ from one another principally in the number of shoes and dies, and the methods adopted for fastening these to the muller and the bottom of the pan. There are also differences in the shape of the mullers and in the method of suspending and raising and lowering them, and the wings fastened to the sides of the pans

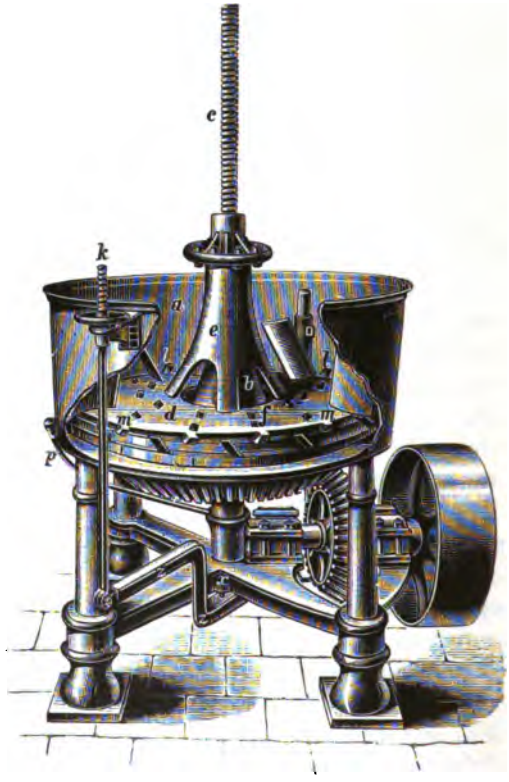


FIG. 449.

assume various forms. A few of the most generally used forms of pan will be found described in the following pages.

The oldest pan, introduced in 1862, and known as the Wheeler pan, is shown in perspective in Fig. 449. The pan *a*, constructed entirely of cast iron, is 5 feet in diameter and 2 feet deep, and has a double bottom for the purpose of heating by steam. The cone *b* is cast in a single piece with the bottom proper. Through this passes the vertical shaft *c*, supported on the bearing at *x*. The muller *d* is

worked from this shaft by means of the driver *e*, which is connected to the shaft by a groove and feather. One of the shoes is shown in Fig. 450, dovetails *f* being cast on them which fit into corresponding openings in the muller. The horizontal grinding surface at the bottom of the pan is formed of eight separate pieces or dies fastened on by dovetails. The distance between the shoes and dies can be regulated by means of the screw *k*, which acting on the lever *z*, raises or lowers the step box in which the shaft rests and works. The vertical shaft *c* is provided with a long screw, by means of which the muller can be raised for cleaning or repairing.

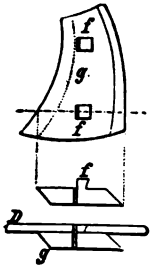


FIG. 450.

The arrangement of a Wheeler pan with wooden sides is shown in Fig. 451. The bottom *b* is made hollow in order that it may be warmed by steam. The cone *z* is cast in one piece with the bottom, *g* is the shaft and *e* the muller fastened to it, *c*, *c* are two of the dies fastened to the pan bottom by dovetails, and *d*, *d* are the shoes similarly fastened to the muller. The shaft is raised or lowered by means of the wheel *r*; *y*, *y* are wings on the pan sides for preventing the pulp from rising too high and for directing the ore mud towards the centre of the pan. A peculiarity of the Wheeler pan is the comparatively large space between the edges of the mullers and the sides of the pan.

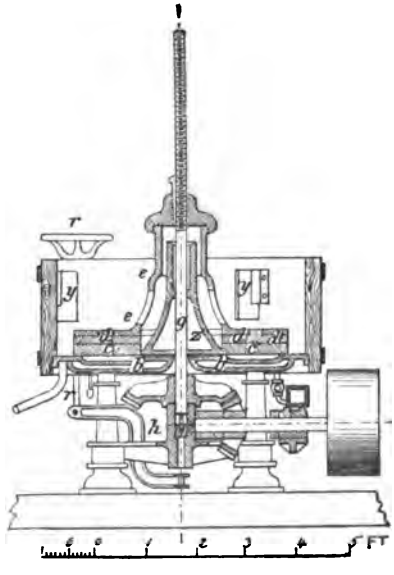


FIG. 451.

The Horn pan is shown in Fig. 452. The pan is of cast iron bolted on to the flat bottom *z*, the dies *s* being fastened to the bottom by dovetails. Below the dies are two channels *k* in the bottom, communicating with each other, and serving for the heating of the contents by steam which enters by the pipe *o* and leaves by the pipe *k p*. The shoes are fastened to the muller in the same way as the dies to the bottom. The muller receives its motion from the driver *f* attached to the central shaft, but the muller is not fastened

to the driver but simply rests upon it; it can be raised or lowered by the screw and hand wheel *w*, the lower wheel fixing it when adjusted to the desired height. *t* and *u* are scrapers fixed at the outer and inner edges of the muller.

The so-called *combination* pan, shown in Fig. 453, is a combination of the pans of Wheeler, Horn and Patton, having wings *l* on the sides provided with copper plates which collect a portion of the amalgam. In such a pan 15 tons of ore can be worked in 24 hours.

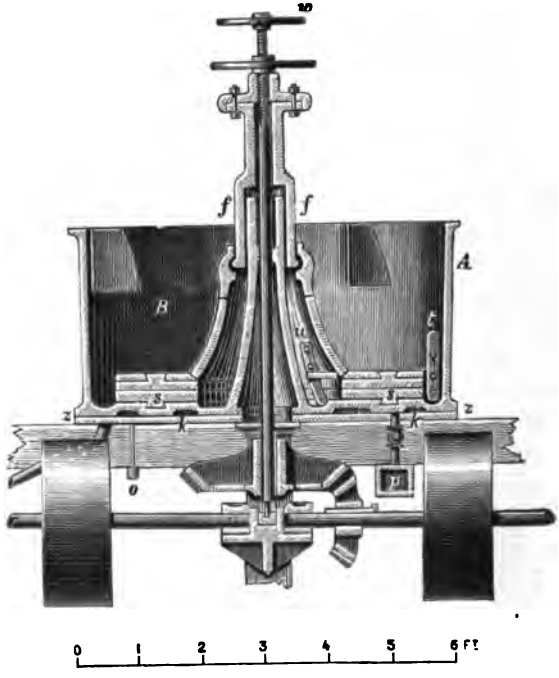


FIG. 452.

The McCone pan is shown in Figs. 454–457, the arrangement of the bottom parts of the pan not greatly differing from those previously described.

A form of pan largely employed in recent times and very favourably spoken of is that of Stevenson, illustrated in Figs. 458 to 461.[1] This pan is furnished with iron mould boards to break up the ore pulp, and these mould boards throw the ore against the pan sides whence it runs down under the muller. The pan is heated by steam circulating below the bottom. The muller is provided with 6

[1] Egleston, *Silver, Gold, and Mercury*, i., p. 379.

shoes, each weighing 100 lbs., and there are 8 dies of iron, weighing 85 lbs. each, the capacity of the pan being 3,500 lbs. of ore. Owing to its comparatively small grinding surface the power required is less than with other pans.

In working the pans, the mullers are first raised about half an inch, water is run in, the muller is set in motion at the rate of from 60 to 90 revolutions per minute, and the ore, varying in weight from 8 cwt. to 2¼ tons according to the size of the pan, is then charged. The charge in a combination pan at the California Mill, Virginia City,

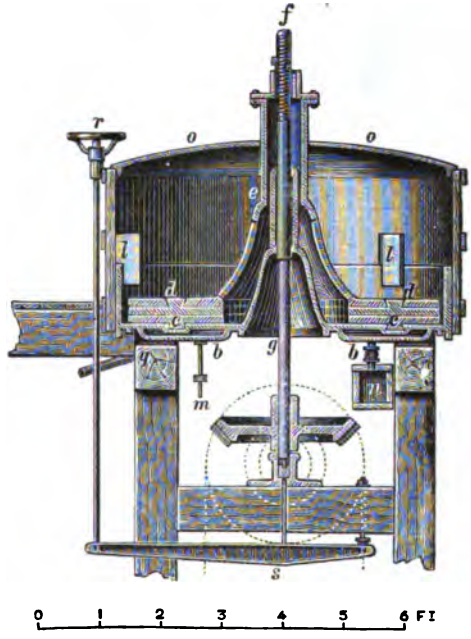


FIG. 453.

amounts to 36 cwt., and in a Wheeler pan, at the Eureka Mill, Nevada, to 32 cwt. The ore and water are stirred together to a pulp which occupies about half the capacity of the pan. As soon as the pulp is uniformly of the consistency of honey the muller is lowered so that the shoes nearly rest on the dies. The ore is now ground fine, the pan being warmed with steam. As a rule two hours' grinding is sufficient, and then the mercury is added. In order to prevent the mercury from being broken up too much, the muller is usually raised about half an inch, and the running is then continued for 3 hours. On an average, the weight of the mercury added amounts to 10 per cent.

of the weight of the ore, and the working of a charge takes from 5 to 6 hours.

The *chemicals* used in the process are generally added at the

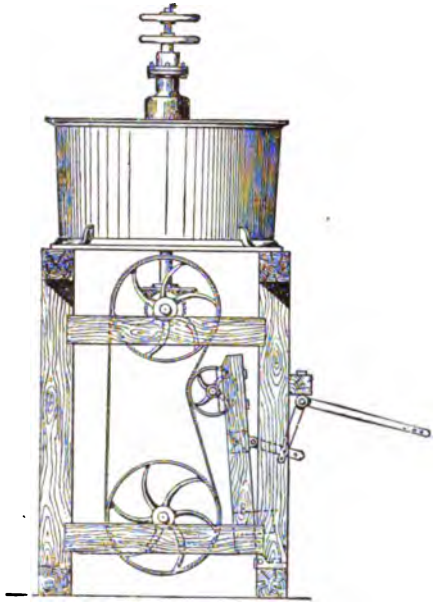


Fig. 454.

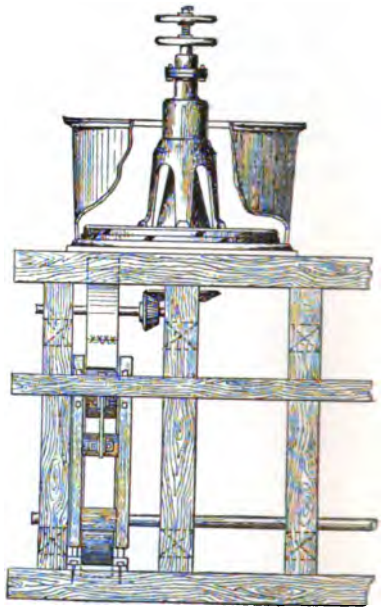


Fig. 455.

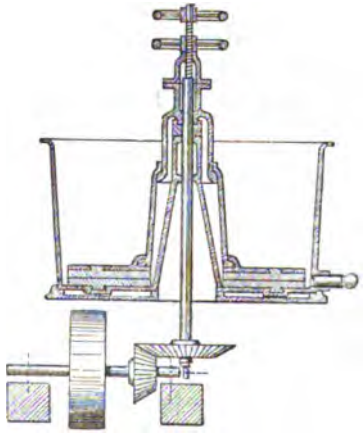


Fig. 456.

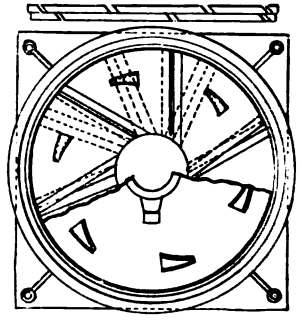


Fig. 457.

same time as the ore, though with many ores they may be entirely dispensed with. Of the very many substances which have been used by the amalgamators working on the Comstock lode, many without

any knowledge of their chemical action, as, for instance, tea anp tobacco leaves—common salt and copper sulphate have proved serviceable, and are still used. The action of these bodies, which is

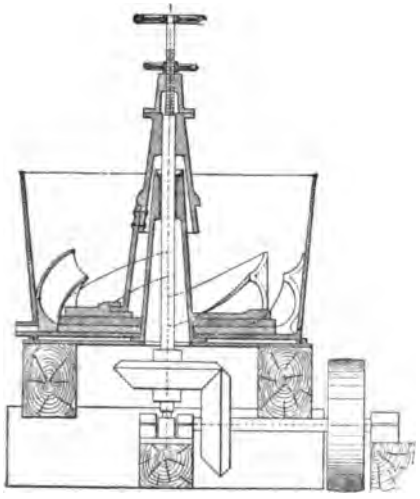


FIG. 458.

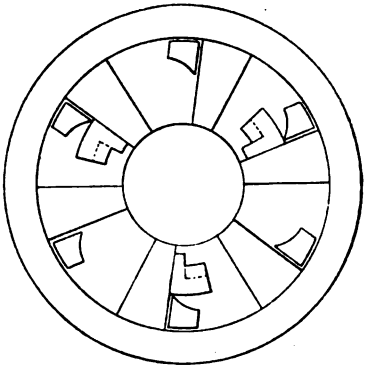


FIG. 459.

the same as in the Kröhnke and Patio processes, has previously been described, and the quantity used varies with the ore. At the California Mill 13 to 18 lbs. of salt and 4½ to 9 lbs. of copper sulphate are added to each charge. At the Consolidated Virginia Mill 6½ lbs. of salt and 3⅛ lbs. of copper sulphate are used.

The metallic iron, which, together with the mercury, liberates silver from the silver sulphide, finds its way into the ore pulp partly

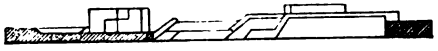


FIG. 460.

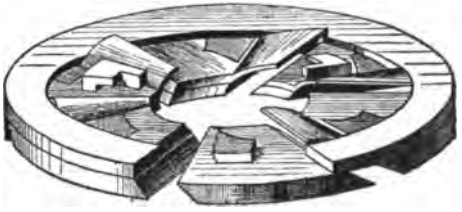


FIG. 461.

through wear of the stamps, the shoes and dies of the pans, and is partly furnished by the substance of the walls of the pan. According to Egleston, from 3⅛ to 6½ lbs. of iron are worn off the stamps for

every ton of ore crushed, and from 7½ to 11 lbs. are furnished by the shoes and dies of the pan.[1]

Of the other chemicals employed, caustic alkalies, soda and potash are used to deprive the ores of any grease that may have found its way in from the machinery, potassium cyanide to purify the mercury, and sodium amalgam to prevent the sickening or flouring of the mercury.

The amalgamation of the silver proceeds very rapidly at first, but its rate rapidly diminishes. According to observations made in the States,[2] after one hour's working in the pan 74·66 per cent. of the silver content of the ore is already amalgamated, at the end of the 2nd hour 76·26 per cent., after the 3rd hour 77·74 per cent., and at the end of the 4th hour 81·04 per cent., no more silver being taken up after this time.

When the amalgamation is finished, the next operation is the emptying of the pan and the separation of the amalgam from the ore. About a quarter of an hour before the emptying, the number of revolutions of the muller is reduced to 40 per minute, and the pan is filled to the top with water. The greater part of the amalgam is either run off first and the rest of the pan contents run into the settler from which the remainder of the amalgam is obtained, or else the entire contents of the pan are run into the settler, and the amalgam and ore separated in the latter vessel. The operation of emptying takes usually about half an hour, water being allowed to flow in during this time.

If most of the amalgam is to be taken directly from the pan, it is drawn off (about 10 minutes after filling up the pan with water) by means of a pipe at the bottom, closed during working by a clamped indiarubber tube, and is then run into an iron reservoir. In this way about nine tenths of the entire quantity of amalgam in the pan may be obtained. A certain amount of amalgam is retained in the spaces between the dies and the shoes and some clings to the pan walls, and this is removed once or twice a month when the pan is cleaned up or when the shoes or dies are changed.

At the California Mill, in Virginia City, 44 pans require the labour of 28 men per 24 hours, viz.—6 amalgamators, 20 men for shovelling the slimes, and 2 mechanics for repairs.

The contents of each pair of pans are run into one settler, and a battery of 5 stamps will supply crushed ore for 2 to 3 pans.

[1] Egleston, *Silver, Gold, and Mercury*, p. 386.
[2] *Trans. Am. Inst. Min. Eng.*, vol. xi., p. 104.

3. The Separation of the Amalgam from the Amalgamated Ores

The complete separation of the amalgam from the amalgamated ore is effected in a settler with revolving arms, a second vessel called an agitator being also used in many cases.

The settler is a cylindrical vat provided with arms, and is from 8 to 10 feet in diameter and 3 feet deep. The bottom is made of cast iron and the walls are usually of wood. The arms are mounted similarly to the mullers of the pans. They consist either of four cross arms of iron fastened on to the driver and provided with shoes like ploughshares, or else of discs of iron similarly fastened and furnished with long radial shoes of wood on their lower sides.

The latter form, which is the one most in use at present, is shown in Fig. 462, where *s* is the disc fastened to the driver *G*, *u u* being the wooden shoes, and the earlier form with shoes like ploughshares is shown in Fig. 463 where *a*, *a* are the arms and *b*, *b* the shoes.

The shoes reach to the bottom of the settler, and can be raised or lowered by an arrangement similar to that used for the mullers. The bottom of the settler slopes towards the sides, and has a groove in which the amalgam collects, and from which it flows by a pipe into a vessel placed outside the settler. This vessel is either fastened directly to the side wall of the settler and emptied from time to time, or else it is placed at a lower level than the settler, and the amalgam can flow continuously from it. The first arrangement is shown in Fig. 463, where *d* is the amalgam reservoir from which the amalgam can be drawn off by opening the plug *f*, whilst in the form shown in Fig. 462 the amalgam flows away continuously. At different heights in the side walls of the settler, openings (*c*, *c*, *c*, Figs. 462 and 463) which can be closed by plugs, are provided in order that the residue suspended in water may be run off.

As soon as the settler has received its charge, consisting of the contents of two pans, it is filled with water to within 6 inches of the brim, the arms making 10 to 15 revolutions, or with coarsely ground ore 20 revolutions per minute. During the first half hour the shoes are kept at a distance of about 8 inches from the bottom, and they are gradually lowered until after the lapse of 2 hours they nearly rest on the bottom. The action of the agitators is to keep the lighter portions of the ore in suspension, whilst amalgam, mercury, undecomposed sulphides, and fine particles of iron collect at the bottom of the settler. The duration of the stirring is so arranged that the settler is empty when the amalgamation of the pan contents

is complete, so that it may be filled again at once, the stirring lasting on an average 3½ hours. At the end of this time the plug of the highest opening in the side of the settler is removed and the turbid

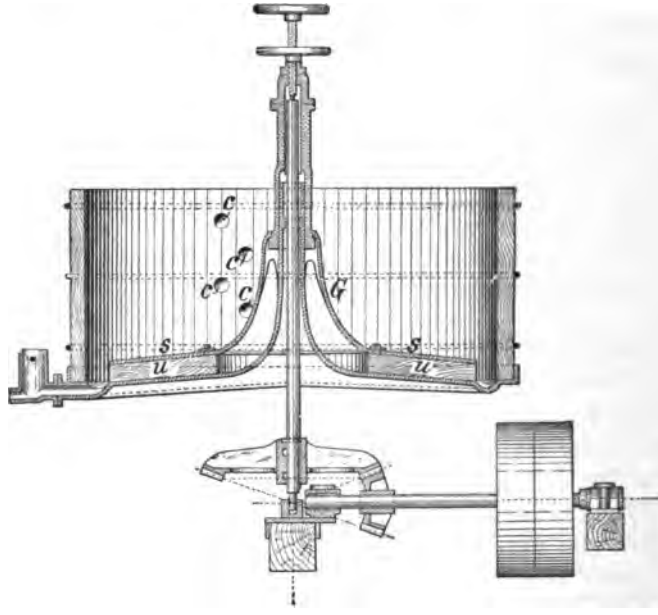


FIG. 462.

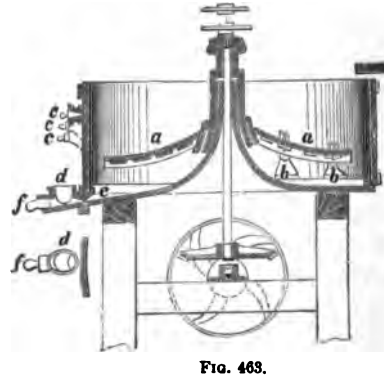


FIG. 463.

liquid allowed to flow away, the agitators being meanwhile kept going, and then the plugs of the second, third, and lowest openings are withdrawn one by one until the settler is emptied of all except the heavier portions above mentioned. The whole operation of emptying

lasts half an hour, and once every week the settler is thoroughly cleaned.

At many large works, the turbid liquid from the settlers is run off into a special wooden tub or *agitator*, in which any portions of amalgam, mercury or undecomposed ore are allowed to settle. These agitators are cylindrical vats of wood 8 to 16½ feet in diameter and 2 feet 6 inches to 4 feet high, one agitator serving as a rule for five or six settlers. The agitating appliance is a driver with four arms at right angles, and to these arms wooden rods are fixed vertically, the whole contrivance making 10 to 20 revolutions per minute. Fig. 464 shows the construction of such an agitator, the screw and hand wheel being for the purpose of raising or lowering the arms. During the stirring, water flows in constantly, and the turbid liquid flows out through an opening at the bottom, the heavier portions remaining on the bottom, whence they are shovelled out at intervals of 3 to 4 days.

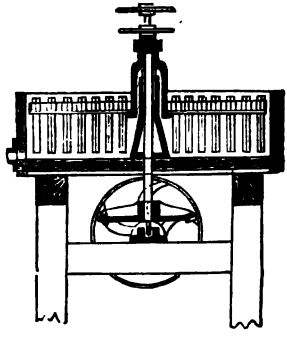


FIG. 464.

Agitators are, however, not generally employed, the liquid and suspended particles from the settlers being usually run over tables or, if the ore in it is valuable, it is worked up in concentrators. At present where extra settling apparatus is considered to be necessary, it is usual to use a modified form of settler in place of the agitator.

4. THE TREATMENT OF THE AMALGAM

The amalgam from the pans and settlers is first deprived of its excess of mercury by filtration through bags of canvas.

All the amalgam which is obtained during the cleaning of the pans and settlers, as well as all other impure amalgam, is first worked up with more mercury in small pans known as clean-up pans before being submitted to filtration.

The construction of one form of clean-up pan, known as the Knox pan, is shown in Fig. 465; this is 4 feet in diameter, is made of cast iron, and has an agitator with wooden shoes fastened to it. The agitator can be raised or lowered by the screw and wheel at the top.

The amalgam is put into these pans and rendered perfectly liquid by the addition of a large quantity of mercury and then stirred up with water for a considerable time (up to 12 hours). In this way

any impurities present in the amalgam are carried off by the current of water, and in many cases these impurities, consisting of unaltered sulphides, are collected and worked up separately.

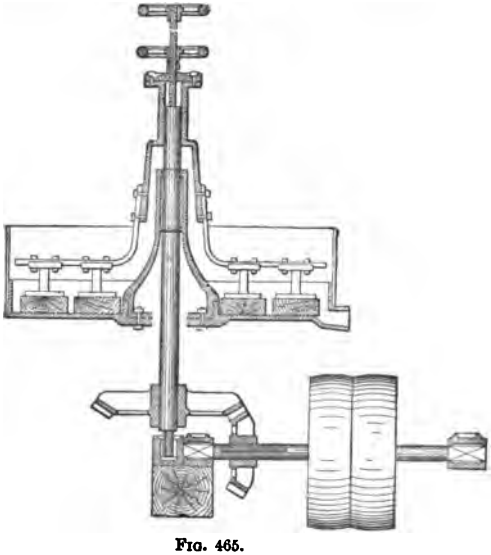


Fig. 465.

The apparatus for filtering the amalgam is a conical bag constructed either wholly of canvas or the upper part of leather and the lower of canvas, being supported in any case by an iron ring at the top. The bags are 10 to 12 inches in diameter at the top and 2 feet to 2 feet 7 inches in length, holding about 12 cwt. of amalgam. The weight of the amalgam itself is sufficient to squeeze most of the mercury through the pores of the canvas. In recent forms of filter the bag is suspended inside an iron cylinder or amalgam safe with a hinged lid secured by a padlock in order to prevent theft. Two

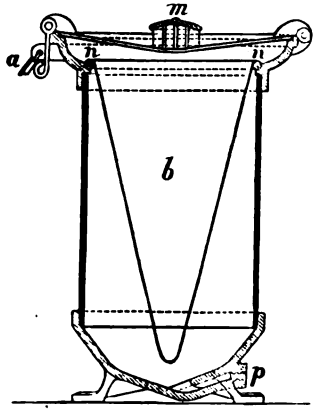


Fig. 466.

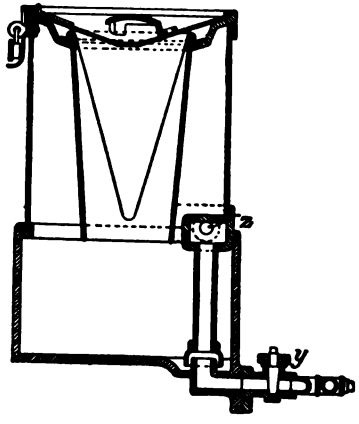


Fig. 467.

forms of amalgam safe are shown in Figs. 466 and 467, the upright cylindrical sides being of wrought-iron plate and the bottom of cast

iron, *b* being the filter or strainer suspended from the iron ring *n*, and *a* the padlock.

The amalgam is run in from the settlers into the bag through a hole, *m*, in the lid of the safe, the excess of mercury forced through the pores of the cloth being drawn off at *p* (Fig. 466), or by the pipe *z* (Fig. 467), the flow being regulated by the tap *y*.

The amalgam remains behind in the bag in the pasty state, and in this condition contains 7 parts of mercury to 1 of silver; but this may be reduced to $3\frac{1}{2}:1$ by squeezing, though in this case the mercury expressed will be very rich in silver.

As a rule one amalgam box is provided for every two settlers below which it is placed, and at the larger works the mercury which drains away flows into a reservoir from which it is raised either by elevators or pumps into another reservoir placed above the pans. From this it flows into smaller reservoirs, each of which supplies two pans, and thus begins its circulation afresh.

An idea of this circulation of the mercury may be gathered from Fig. 468, which shows the arrangement used at the Consolidated

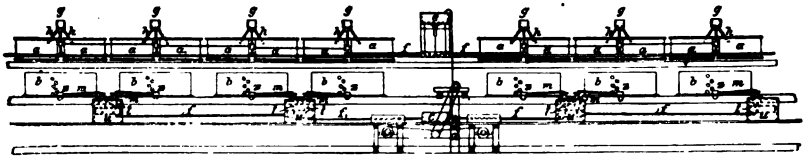


Fig. 468.

Virginia Mill, Virginia City, Nevada (Egleston). The fresh mercury is poured out from the iron bottles into the lower reservoir *c* and pumped from this into the upper reservoir *e* by means of a mercury pump *d*. From this reservoir it flows by a vertical pipe not shown in the figure into the horizontal pipe *f*, and from this into the smaller containers *g* placed above the pans *a*. One container supplies mercury for two pans through inclined tubes *h*, and from the pans the mercury or amalgam flows into the settlers *b* and into the collecting boxes *z* placed in front of them. From these it passes along tubes *m*, which are placed slopingly so as to restrict the pressure of the mercury, into the amalgam strainers *u* with their canvas bags *t*, and from these it passes along the pipe *f* into the reservoir *c*, whence it is pumped up to *e* to begin the circulation again.

The raising of the mercury from the lower to the upper reservoir is effected either by pumps or elevators, preference having lately been given to the latter.

The details of the construction of a mercury pump are shown in

Figs. 469 to 471. The pump has a steel plunger x, and the gland is packed with rubber dipped in melted tallow, with water in the lower part of the stuffing-box. The valves are of rubber, fitting easily, and the plunger runs in hydraulic packing, so that the mercury is prevented from being floured by the pump. Below the pump is a box

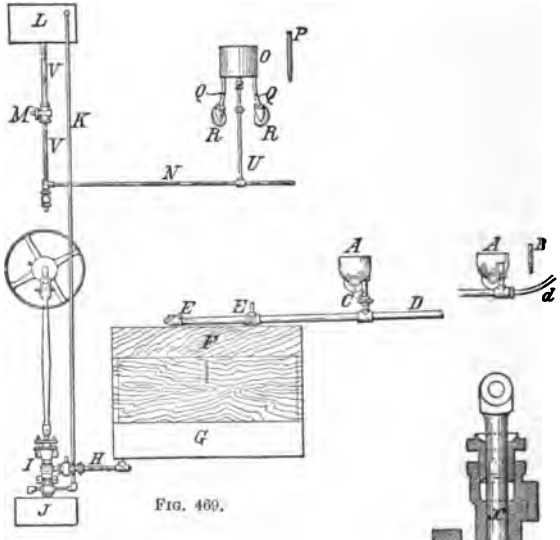


FIG. 469.

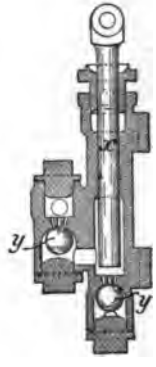


FIG. 471.

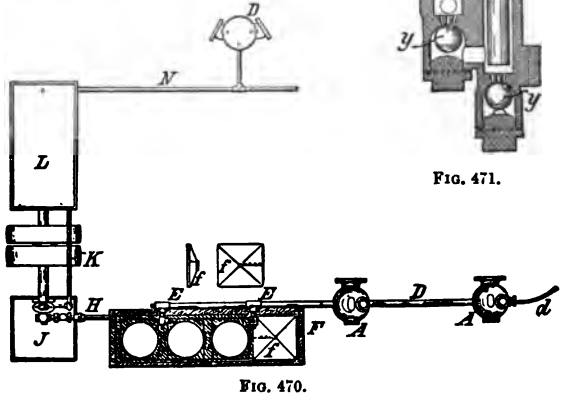


FIG. 470.

J to catch any leakage. The mercury which is to be raised by the pump flows from the iron tank G into which it drains from the amalgam filter and enters the pump through the pipe H. The pump plunger has a 5-inch stroke and makes 40 strokes per minute, the mercury being forced up the vertical pipe K, $\frac{3}{4}$ inch in diameter,

into the reservoir *L*. By means of the vertical 1 inch pipe *V*, provided with a stop-cock *M*, the mercury enters the horizontal pipe *N* and thence rises up through *U* into *O*, which is one of the smaller containers supplying mercury to two of the pans; the supply of mercury to these particular containers can be cut off by inserting the plug *P* into the mouth of the tube *U*. The tubes *Q* convey the mercury to the pans; *A* is one of the mercury bowls attached to the bottom of the settlers, and from it the mercury and amalgam

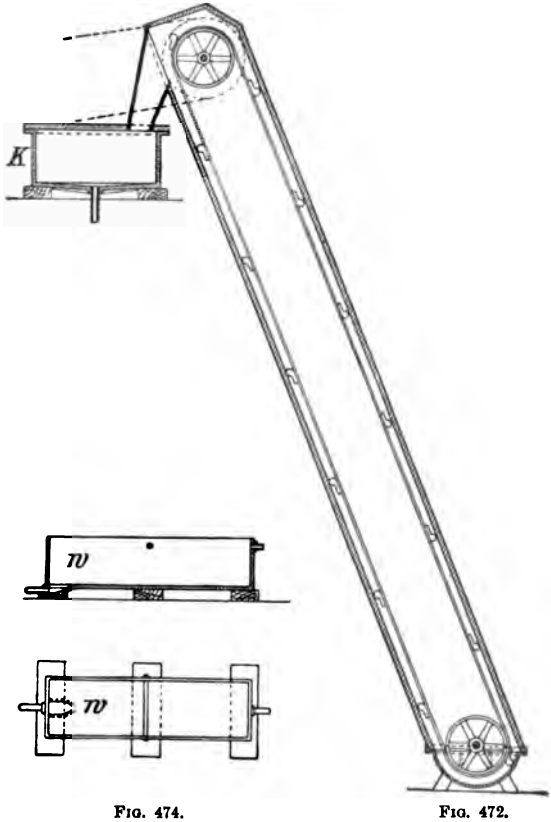


Fig. 472.

Fig. 473. Fig. 474.

flow by the horizontal pipe *D* and the smaller vertical pipes *E* into the filters placed inside the wooden box *F*. There are four canvas filters to each box, and the mercury from all of them collects in the iron tank *G*, which is 5 feet long, 12 inches deep, and 18 inches wide, flowing again to the pump and so on through the system.

The pipe *d* is a prolongation of *D*, and serves to introduce steam into the latter, whenever it needs cleaning out.

The mercury elevator (Fig. 472) resembles an ordinary belt

elevator, and is encased in sheet iron. The buckets are of the shape shown in Fig. 472. The reservoir from which the mercury is lifted is shown at *w* in Figs. 473 and 474, and is made of cast iron, the receiving vessel *K* being constructed of the same material.

The amalgam which remains behind in the filters is heated in the cast-iron retorts to be subsequently described. The loss of mercury in the Washoe process is from 1 to 3½ lbs. per ton of ore, the loss being partly chemical and partly mechanical.

Mechanical losses of mercury are caused by the presence of minerals of high specific gravity, such as cerussite, which carry mercury away with them, by aluminium and magnesium silicates which coat the globules of mercury, by grease and fat, by the flouring of the mercury in the stamping, grinding and washing, and by volatilisation. When copper and lead sulphides are present in the ores, or if too much copper sulphate is added in the pans, the amalgam produced, though of a pasty consistency, is easily broken up into very fine globules.

The chemical loss is chiefly due to the conversion of some of the mercury into sulphide, owing to the presence of silver sulphide in the ores, and to a less degree to the formation of mercurous chloride, as the latter is chiefly reduced again by the iron present to the metallic state.

The yield of silver in the Washoe process varies with the character of the ore from 70 to 80 per cent. of the assay content of the ore.

5. The Treatment of the Ores after Amalgamation

The residues which are suspended in the muddy liquid run out of the settlers and agitators, form what are known as *tailings*, and contain a certain amount of unaltered ore, which in the majority of cases can be profitably worked.

The solid portion is therefore either collected in large tanks, and then dressed, or else the mud is led directly over tables (blanket sluices) in which the heavier portions are collected. The blanket tables have so far proved to be the best and cheapest arrangement for collecting the heavier portions of the tailings, and are especially used in Nevada. They are made of wood with sides from 2 to 3 inches high, are 20 inches wide, and as much as 1800 feet long, with a slope of 6 to 10 inches in 12 feet, and are usually placed side by side, sometimes only two or three together, or in some cases there are as

many as 15 or 20. The bottoms of the sluices are covered with coarse blankets, and the latter can be easily taken out and washed in the case of short sluices, but in longer ones they are tarred on their under sides and nailed in position.

The stream of turbid liquid running along the sluices deposits the heavier portions of its contents on the blankets, and in the case of short sluices these are periodically taken out and washed. With long sluices the tailings are brushed at intervals into slots, through which they are run off into sluices at a lower level and so on to the collecting tanks.

According to Egleston,[1] the pulp from the agitators at the Eureka Mill, Eureka, Nevada, first flows into reservoirs from which it is raised by an Archimedean screw into a wooden tank, 10 feet long, 12 inches wide, 16 inches deep. From this it flows through 6 sluices lying side by side, each 1200 feet long, 20 inches wide, and 3 inches high, the sluices being separated by boards half an inch thick. The sluices are covered with coarse blankets 10 feet long, fastened by tacks and cleats. At intervals of 200 feet there are slits 3 inches wide across the bottom of the sluice, which are covered with sheet-iron covers whilst the pulp is flowing over them, and which communicate with a trough underneath the sluice. As soon as a certain amount of ore has collected on the blankets the covers are removed (every 4 or 6 hours) and the ore swept with brushes into the slits. In this way 6 tons of ore are recovered daily with the labour of 3 men, and the recovered ore is treated in the same way as the original ore.

The largest concentrating plant of this description is that known as the Woodworth Sluices at Dayton, in Nevada, and described by Egleston.[2] Here the tailings from 25 to 30 amalgamating plants at Gold Cañon, where there are 262 stamps, each of a capacity of 2 tons daily, are concentrated. The pulp from the different works is brought along a channel 3½ miles long and 18 inches square to the Woodworth Sluices. The pulp flows first into reservoirs and from these into distributing boxes with a sliding gate for each sluice. There are twelve of these placed side by side, 1700 feet long, 19 inches wide, and 3 inches deep, with a fall of 1 inch in 8 feet. The blankets are tarred on their under sides and fastened to the bottom of the sluice. At intervals of every 150 feet there are cross slits, 3 inches broad and 17 inches long, into which the heavier ore remaining on the

[1] *Op. cit.*, vol. i., p. 449.

[2] *Engineering*, 1880, vol. xxx., pp. 395 and 451; *Metallurgy of Silver, Gold, and Mercury*, vol. i., p. 450.

blankets is collected, and whence it flows along a trough below into reservoirs. Fresh water is allowed to flow in at various stages along the sluice, and the top portions are swept every 8 hours, the lower portions at intervals of 12 hours. In each day, 12 tons of ore are concentrated, and the labour of 17 men is required for each 12 hour shift. The concentrates are worked up at the Woodworth Mill in Horn pans with salt, copper sulphate and mercury, and 70 per cent. of the assay content of the silver is recovered.

As previously mentioned the various parts of the plant required for the Washoe process are arranged in terrace form to avoid cost of transportation of material, and the method of arrangement may be gathered from Fig. 475. The ores come in at the highest level *H*

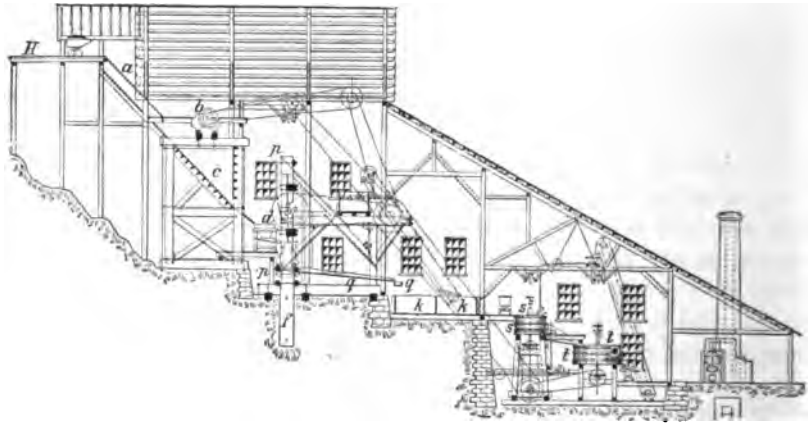


Fig. 475.

and are thrown down the inclined grizzly *a*. Pieces larger than walnuts pass on to the floor where the stone breaker *b* is situated, whilst smaller pieces fall through the grizzly and into the ore bin *c*, where the crushed ores from the stone breaker are also received. From the bin the ores pass to the automatic feeder *d* supplying the stamps *p*, the pulp flowing along *q* to the reservoirs *k* in which the heavy ore settles. The deposited pulp is then transferred to the pans *s*, in which the amalgamation takes place. After sufficient amalgamation, the pan contents are allowed to flow into the settlers *t* in which the amalgam is separated from the remaining ore, the latter being either further treated by agitators, blanket sluices or vanners, or else run to waste.

The following table of Egleston's gives the details of various

plants used for the Washoe process as regards their capacity, size, and power consumption.[1]

	10 Stamp Plant. Capacity, 18 to 20 tons in 24 hours.		20 Stamp Plant. Capacity, 40 tons in 24 hours.		60 Stamp Plant. Capacity, 130—140 tons in 24 hours.	
	Number of each.	Horse-power used.	Number of each.	Horse-power used.	Number of each.	Horse-power used.
Blake's stone breakers .	1	6	1	6	1	5·5
Self-acting feeders . .	2	—	4	—	—	—
Stamps, each weighing 825 lbs., 90 drops per minute	10	12	20	23	60	67·5
Pans, each 5 ft. in diameter.	6	30	12	60	28	112
Settlers, each 8 ft. in diameter.	3	9	6	18	14	28
Concentrators.	—	—	—	—	3	6
Power lost in friction .	—	7	—	13	—	25
Total horse-power . .	—	64	—	120	—	244

The engines for the 60 stamp plant in Nevada are of such a size as to be capable of doing double the work ordinarily required of them.

As regards the consumption of water in the Washoe process, according to Egleston, it may be taken at 7½ gallons per horse-power per hour for the boilers, 72 gallons an hour for each stamp, 120 gallons an hour for each pan, and 60 gallons an hour for each settler.

If the water from the stamps, pans and settlers, is collected in settling tanks, it may be used over again, with an average loss of 25 per cent. Altogether the consumption of water for each ton of ore treated may be taken at 2000 to 2500 gallons.

Modifications of the Washoe Process

The Washoe process has in some cases undergone alterations, and the two chief ones in use are the *combination* process, in which the ores are submitted to a preliminary concentration before being amalgamated, and the *Boss* process, called after Boss the inventor, in which the amalgamation is not conducted in a single pan, but in a series of pans through which the pulp flows continuously.

[1] *Op. cit.*, p. 443.

The Combination Process (Concentration and Amalgamation)

This process may be employed with advantage in the case of ores which cannot be worked directly by the Washoe process, as is the case when they contain galena, blende, copper and iron pyrites (which act injuriously upon the amalgamation), and which are still not rich enough to pay for a preliminary chloridising roasting. The method is also applicable to ores carrying gold and silver, in which the above sulphides are present.

In this process the ores are crushed in stamp mills and then concentrated on Frue vanners. By this means the refractory sulphides are separated, and the tailings obtained are suitable for treatment by the Washoe process. They are run into settlers and afterwards taken out and amalgamated in pans. If the ore is auriferous, mercury is charged into the mortars of the stamp battery, and the pulp is led over amalgamated copper plates, which retain the gold amalgam and any free gold still present, after which the pulp goes to the Frue vanners. The sulphides or concentrates from the vanners may be worked up in a variety of ways (chloridising roasting and amalgamation, chlorination, or smelting so as to obtain the precious metals alloyed with lead), and are sold to other works for that purpose.

This combination process is employed with advantage in various works where the simple Washoe process had not proved suitable. Places where it is in successful operation are the works of the Montana Co., Ltd., at Marysville, Montana, where auriferous silver ores are worked, those of the Combination Mining and Milling Co., at Philipsburg (Montana), at the Lone Pine Mine, and Maginiss Mine, Montana, and at the works of the Webster Mining and Milling Co., Marysvale, Utah. The ores of the latter company contain 8 per cent. of lead in the form of cerussite and galena, and the concentrates from the vanners contain 50 per cent. of lead with considerable amounts of gold and silver, and are sold to the smelting works, 85 per cent. of the precious metals in the ore being obtained from them.

The Boss Process

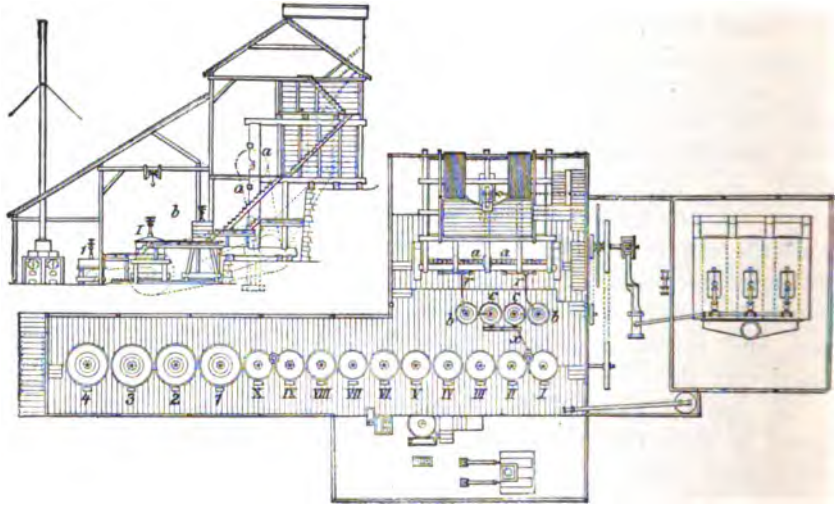
In the Boss process the ore pulp from the stamp mills is first finely ground in pans, and then flows through the whole series of amalgamating pans and settlers. By this means the costly labour of transferring the pulp from the settling tanks to the pans is avoided, and the pulp is worked not in one pan, but in all the pans of the plant, and is thus maintained in intimate contact with the mercury for a long period. The pans in which the fine grinding takes place

are usually placed in front of the stamps, the pulp flowing along a pipe from the mortar boxes into the pans, of which there are two, one below the other, serving for 10 stamps. The pulp flows from a hole in the bottom of the first into the second pan, where the fine grinding is finished. After the fine grinding the pulp flows through the entire series of amalgamating pans placed one beside the other and then through all the settlers arranged in the same way on the same level. Each pan is furnished with an overflow pipe through which the pulp flows, connecting it to the next one of the series, and the last pan is connected in a similar way with the first settler, and so on, so that the pulp entering the first amalgamating pan flows away at last from the last settler. Each pan and settler can if necessary be thrown out of the series, an arrangement being provided whereby in this case the contents can be transferred by steam pressure to the next pan or settler in operation. The quicksilver is distributed automatically, as above described. The amalgam is collected in receivers, one for each pan and settler, and from these it is led to the canvas filters previously described.

A general view of the plant used in the Boss process is given in Figs. 476, 477 and 478. The ores are sized as previously mentioned, then crushed and brought to the mill *a*, which in this case consists of 20 stamps. The pulp from each 10 stamps flows through the pipe *r* into the grinding pan *b* and then into the similar pan *c*. The pulp from both sets of pans passes along the pipe *x* into the first amalgamating pan, and flows through the entire series of pans *I* to *X*. From the pan *X* it passes to the first settler *1* and then though settlers *2*, *3*, *4*, and is afterwards either run to waste or worked up in concentrators. The agitators of the pans and settlers are worked from the shaft *y* by means of clutch coupling, and the pans are heated by steam circulating in a double bottom. The pulp in the Boss process must be comparatively thinly fluid. The advantages of the process as compared with the ordinary discontinuous amalgamation process are a smaller cost for labour, a smaller consumption of water, fuel and mercury, and a higher yield of silver. It is said to have given good results in California and Mexico, but the author is not aware that any recent communications have been published concerning it.

That the Washoe process is a very suitable one for ores containing native silver and silver chloride is evident from the results obtained in Nevada at White Pine, and in Utah at Silver Reef.

Quite recently a plant has been erected at Broken Hill, New South Wales, for working quartzose and clayey ores containing native silver with chloride and iodide. This plant has special pans for fine grinding and special amalgamating pans. There are 60 stamps and 24 grinding and amalgamating pans of cast iron of a diameter of 4½ feet and a height of 3 feet. The mullers of the



FIGS. 476 and 477.

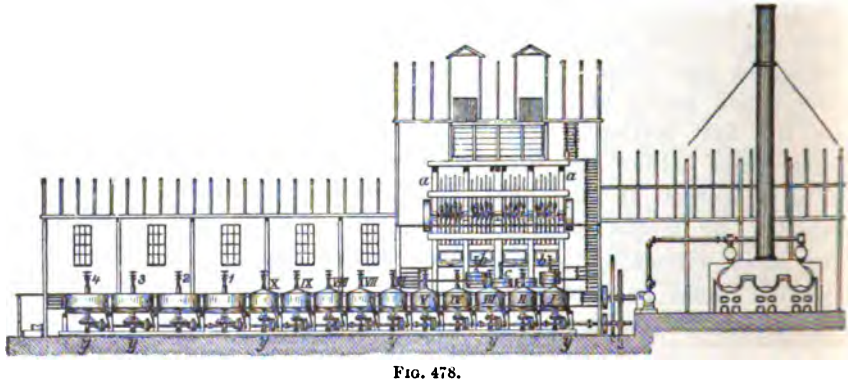


FIG. 478.

grinding pans make 40, and of the amalgamating pans 80 revolutions per minute. There are 12 settlers with cast-iron bottoms and wrought-iron sides, each being 5 feet in diameter and 3 feet 3 inches high, the agitators in them making 14 revolutions per minute. It was expected that this plant would work up 200 tons of ore daily, but this figure has not been reached.

Amalgamation with Reagents preceded by a Chloridising Roasting

In this process the silver present in the ore is first converted into chloride by roasting with salt, the silver chloride is then reduced by metallic iron or copper, and the reduced silver amalgamated.

The chloridising roasting of the ore is carried out in reverberatory furnaces, and the reduction of the chloride and the amalgamation of the silver is effected in some form of amalgamating apparatus (barrels, pans or *tinas*). The various methods of amalgamation are: (1) Barrel amalgamation, also known as the European amalgamation process; (2) Pan amalgamation (Reese-river process), and (3) *tina* amalgamation (Francke-Tina process).

The method is applicable to many ores which cannot be worked directly by the Washoe process. The ores mainly worked are those containing mixed sulphides of silver and other metals, particularly antimonial and arsenical sulphide ores, as well as those containing silver sulphide together with sulphides of iron, copper, zinc and lead. If, however, the amount of galena present is over a certain limit, the ores are rendered unsuitable for treatment by this process.

In Europe, the method only remains in use in a few places, but in America it is extensively employed, and has in recent times reached a high degree of perfection.

For the operation of chloridising roasting, it is necessary that the ores should be in the state of fine powder and perfectly dry, as if they are at all damp they form lumps with the salt, and perfect roasting becomes impossible. The ores are therefore usually stamped in the dry state and dried previous to stamping, or if wet stamping must be used, they must be dried afterwards. In any case the ores are broken up in stone crushers before stamping.

The various operations to be considered are:

1. The drying and crushing of the ore.
2. The chloridising roasting.
3. Barrel amalgamation.
4. Pan amalgamation (Reese-river process).
5. *Tina* amalgamation (Francke-Tina process).

1. The Drying and Crushing of the Ores

As a rule the ores are first dried and then submitted to dry stamping, or if wet stamping be used they are dried after that operation.

If the ore is delivered ready broken it is dried at once, otherwise

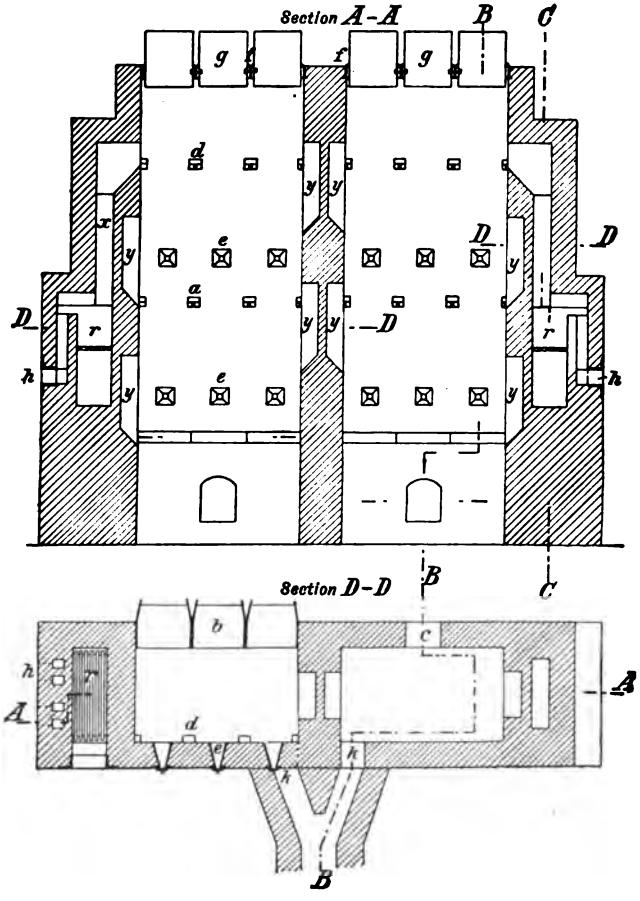
it is broken in stone crushers before being dried. The drying operation may be conducted either on cast-iron plates or in a special drying furnace, the use of cast-iron plates which are generally heated by waste gases from the roasting furnace being more tedious and requiring more labour than the employment of a special furnace, and being in addition injurious to the health of the workpeople owing to the inhalation of the ore dust. Since the year 1873 such drying arrangements have no longer been erected, and all the newer works use drying furnaces. As types of the furnaces in use in the model works of the United States the horizontal rotating cast-iron cylinder and the Stetefeldt drying furnace may be described.

The rotating cylinder or revolving ore dryer is usually arranged in the same way as the continuous roasting furnace previously described; it is made of larger diameter at the fire end—viz., 3½ feet diameter at the wide end and 3 feet in diameter at the smaller end, and is 18 feet long. The ore is fed in at the narrower end and travels gradually towards the fire end, shelves or wings of sheet iron arranged spirally inside mixing the ore and assisting its movement. The fire grate is at the wider end and the flue at the charging end, and the ore is fed in and withdrawn continuously, falling as it leaves the cylinder at the fire end into a pit whence it is taken while still warm by an elevator to the automatic ore feeders supplying the stamps. The cylinders are capable of drying from 30 to 40 tons of ore in 24 hours.

The Stetefeldt drying furnace is somewhat similar to the earlier roasting furnace of Hasenclever (page 56), and consists of a shaft containing a series of cast-iron plates, of which the alternate ones are parallel to each other, the plates being set at an angle of 38°. The ore charged in at the top, on the top plate, rests upon it until its angle of repose is exceeded, when it begins to gradually fall down on to the next lower plate, and so on until it reaches the last plate which projects from the furnace; it slides along this and finally falls into a receiver. The furnace is heated by a fireplace at the side and the products of combustion pass from above downwards, entering at the top and passing first over each plate and then under it, channels in the narrower side walls of the furnace enabling the gases to pass round each plate. At the under side of the lowest plate the waste gases pass to a chimney with a powerful draught. The passage of the hot products of combustion through the furnace in this direction is necessary, as in this way the hot gases come first in contact with damp ore and are so cooled that they do not act destructively upon the iron plates; further the moisture given up to the gases from

the ore is prevented from condensing as the gases come into contact with hotter ore as they pass down through the furnace.

The construction of the furnace is shown in Figs. 479 to 482, where g is the charging opening for the ore, and a, a are the cast-iron plates on which the ore falls; r, r are the fireplaces, and h, h the



FIGS. 479 and 480.

openings for air. From the grate the hot products of combustion pass along the flue x, and enter the furnace at the top above the first plate, and proceeding in a downward direction, leave the furnace by the chimney flue k. The openings y, y in the walls of the narrower sides of the furnace allow the gases to make their way round the ends of the plates; e, e are openings for clinkering in the event

of any stoppage taking place. The height of the furnace to the top of the hopper is 21 feet, and the shaft measures 7 feet by 4.

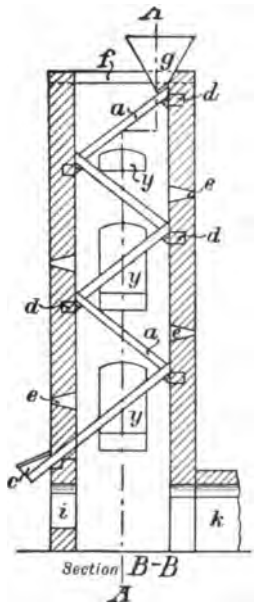


Fig. 481.

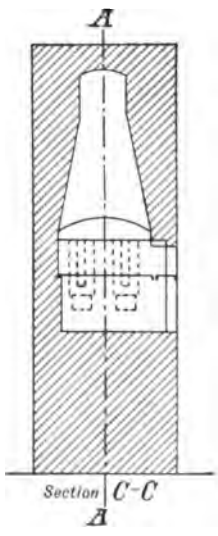


Fig. 482.

In this furnace, which the author witnessed at work at the Lexington Mill, Butte City, Montana, not only ore but salt was also dried, the furnace drying 15 to 25 tons of ore, or 6 to 8 tons of salt per 24 hours, one attendant being necessary for each shift, and one cord of wood being burnt in the 24 hours.

The ore may be pulverised in any of the various forms of mill (edge runners, *arrastras*, ball mills or stamps), but in the United States the Californian stamp mill previously described is the most generally used. The ore whilst still warm is carried from the drying furnace by an elevator with iron buckets, and charged into the hoppers of the automatic ore feeders supplying the stamps. The mortars of the stamp mills are either of the single or double discharge type, the screens being made of brass wire gauze of 30 to 100 meshes per linear inch. A mortar for dry crushing with double discharge is shown in Fig. 483, where *a* is the feed shoot and *b*, *b* the screen frames. From the mortar the crushed ore is carried to the elevators by archimedean screws and raised to the charging level of the roasting furnace. The ele-

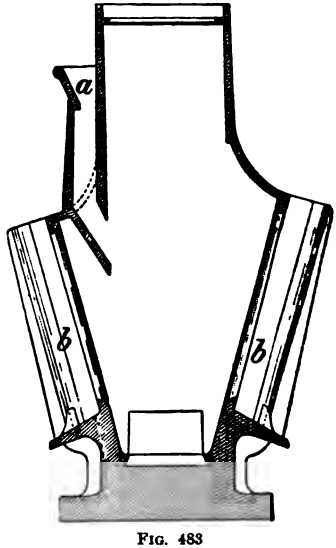


Fig. 483

vators are of the belt form, shown in Figs. 484 and 485, and consist of a series of iron buckets *a*, fastened to an endless belt; to prevent the scattering about of the ore the elevator is cased with wood.

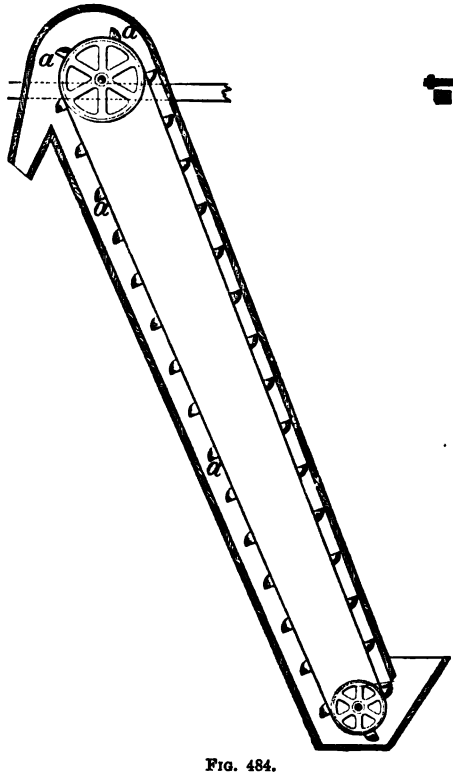


FIG. 484.

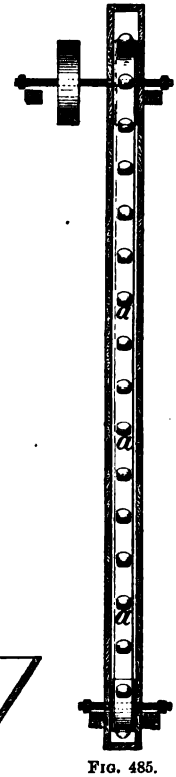


FIG. 485.

Particulars of the size and capacity of some of the stamp mills in the United States will be found in the following table of Egleston's:[1]

	White Pine, Stanford Mill.	Pioche, Raymond and Ely Mill.	White Pine, International Mill.	Butte City, Lexington Mill.
Number of mortars	6	6	6	10
Single (1) or double (2) discharge	2	2	2	1
No. of stamps in each mortar box	5	5	5	5
Total number of stamps	30	30	30	50
Weight in pounds of each stamp	750	750	750	850
Height of drop in inches	8	8	7½	7—8
Number of drops per minute	95	95	93	94
Tons of ore crushed in 24 hours	52	48	33	60
Capacity of each stamp in tons per 24 hours	1·73	1·6	1·1	1·2

[1] Egleston, *Gold and Silver*, ., p. 185.

2. The Chloridising Roasting of the Ores

This operation consists in roasting the ores with salt; a necessary condition is that such ores as contain no peroxide of manganese must contain a certain quantity of pyrites, but not too much, otherwise they would form sulphates and free sulphuric acid in the roasting, and decompose some of the salt. If the ores contain too small a quantity of pyrites, bodies are added which would form sulphuric acid when roasted, such as coarse matte, copper or ferrous sulphates, and if too large an amount is present the ores are roasted first without any addition of salt.

The amount of pyrites or of coarse matte necessary for the roasting operation varies according to the character of the ores from 6 to 30 per cent. When the amalgamation process was in use at Freiberg, ores were roasted with 20 to 30 per cent. of raw matte, whilst in many works in the States only 6 to 10 per cent. suffices. Ores containing manganese peroxide do not need the presence of pyrites for a chloridising roasting.

The amount of salt requisite for roasting depends chiefly upon the character of the ore, and also upon the arrangement used for roasting and the manner in which the process is worked. Pyrites, zinc blende, calcite, dolomite or fluor spar require sulphuric acid or chlorine to decompose them, and consequently increase the amount of salt necessary. According to the amount of these bodies present, the amount of salt required varies from 3 to 20 per cent. of the weight of the ore. If large amounts of pyrites are present, the ores are submitted to a preliminary roasting, and thus the excessive consumption of salt is avoided.

The chloridising roasting is also an oxidising roasting, the sulphides present being converted into oxides and sulphates. The sulphates produced in part react upon the salt, forming metallic chlorides and sodium sulphate, and in part are decomposed by heat into oxides and sulphuric anhydride. The sulphuric anhydride so produced reacts upon common salt and liberates chlorine. If moisture is present, sulphuric acid is produced, which gives rise to hydrochloric acid by its action upon the salt.

The free chlorine converts compounds of metallic sulphides with arsenic and antimony sulphides into metallic chlorides with the production of chlorides of sulphur, arsenic and antimony.

The hydrochloric acid formed converts any metallic oxides, sulphates, arseniates and antimoniates present in the ores or produced in the roasting, into chlorides; water, chlorine and chlorides of sulphur, arsenic or antimony are simultaneously produced.

Volatile chlorides are produced by the reaction between the sulphates and the common salt present, as well as by the action of chlorine and hydrochloric acid upon these bodies. Of these chlorides, those of copper and iron give up a portion of their chlorine to metallic silver, metallic sulphides, arsenides, antimonides, arseniates, antimoniates and sulphates, the cupric and ferric chlorides being reduced to cuprous and ferrous salts.

The product of the roasting operation contains the greater part of the silver as chloride, together with some unaltered silver ore, silver arseniate and antimoniate, the iron chiefly as oxide with some ferrous and ferric chlorides and sulphate, the manganese, copper and zinc as oxides, sulphates and chlorides, the lead as oxide, sulphate and basic chloride, and nickel and cobalt as oxide, sulphate, chloride and arseniate.

Where the roasting is carried on in reverberatory furnaces, with fixed hearths and hand labour, three stages of the roasting operation may be distinguished, namely, the kindling period (*anfeuern*) the desulphurising period (*abschwefeln*), and the final roasting (*gutrösten*). The kindling period is the beginning of the operation; in the second, *abschwefeln* or oxidation period, sulphates are produced from the sulphides; in the *gutrösten*, by increasing the temperature, the decomposition of the salt and the formation of silver chloride takes place. In continuous working furnaces with rotating cylinders, or of the Stetefeldt type, which are usually employed at the present time, these distinct stages are not clearly marked.

At the present time it is not usual to continue the roasting in the furnace until all the silver is converted into chloride, but the charge is withdrawn in a hot condition before this stage is reached, and during the gradual cooling, extending from 12 to 30 hours, a further chloridising takes place, and the silver in the ore, not existing as chloride (which may amount to 40 per cent. of the silver content of the ore), is gradually converted into that salt.

By the chloridising in the furnace and this subsequent action, 95 per cent. of the silver in the ore may be converted into silver chloride.

The operation of chloridising is chiefly conducted in reverberatory furnaces, muffle furnaces only being occasionally used, on account of their excessive consumption of fuel. Shaft furnaces are also used.

The various forms of reverberatory furnace with fixed heating chambers in use for this purpose, are: the ordinary short furnace with single and double hearths, the *fortschaufelungs* furnace or long-bedded calciner and the O'Harra furnace; the furnaces of Brückner,

White, and Howell have rotating hearths, and the Stetefeldt furnace is the only one in use of the shaft type.

The continuous *fortschaufelungs* furnace and the O'Harra furnace, figured and described in the articles on copper and lead, have the advantage over the shorter furnaces which work intermittently, in that they have a greater output and consume less fuel, but even these have been replaced in the States by rotating cylinder furnaces and Stetefeldt's shaft furnace. In these furnaces the roasting proceeds independently of the workmen, and enables the chloridising to be conducted very completely with a comparatively small consumption of fuel and labour.

The first furnace of this kind was the Brückner cylinder working discontinuously, described on page 80. At first this furnace was provided with a diaphragm, in order to stir up the ore more completely, but this proved unsuitable and was done away with. The Brückner

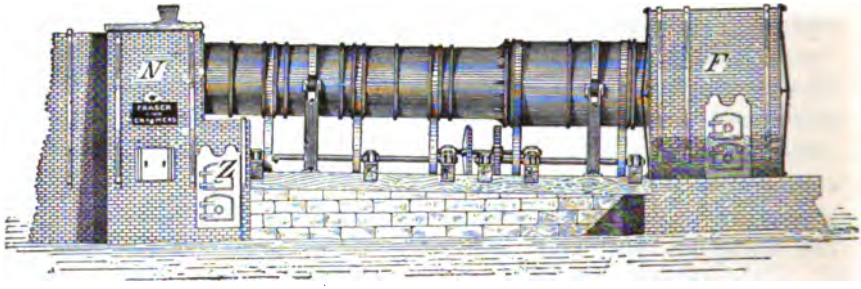


FIG. 486.

furnace was followed by the continuous acting White furnace, described on page 81, and this was further improved by Howell, the White-Howell furnace being shown in Fig. 486. This differs from the previously-described White furnace, in that the rotating cylinder is made wider at the fire end than at the flue end for the third of its length, and this wider portion is lined with fire-brick, the narrower part being of cast iron only. Projecting cast-iron ribs in the cylinder lift up the ore, carry it round and drop it through the flames. An auxiliary furnace, as in the White furnace, is often placed at *Z* for heating the flue dust or to assist in the after chloridising. The furnace is made from 24 to 27 feet long, and 3 to 4 or 4½ feet in diameter, the capacity of the smaller furnaces (24 feet by 3 feet) being 15 to 20 tons, of the medium size (27 feet by 4 feet), 20 to 30 tons, and 30 to 45 tons per 24 hours in the largest sized furnace (27 feet by 5 feet). The White furnace previously described is of similar

dimensions to the White-Howell furnace, and works similar amounts of ore.

In the Brückner furnace, as a consequence of the working being intermittent, the amount of ore roasted in a given time is smaller than with the White and White-Howell furnaces, whilst the fuel consumption is greater. From 3 to 10 tons of ore, according to its character, can be roasted in 24 hours in the Brückner cylinder, and 96 per cent. of its silver content converted into chloride. In the White-Howell furnaces the salt must be added together with the ore, but in the Brückner furnace it can be added later. The fuel consumption per ton of ore is 900 lbs. in the Brückner furnace, 600 lbs. in the *fortschaufelungs* furnace, 300 lbs. in the White and Howell, and 200 lbs. in the Stetefeldt furnace, the chlorination being the same in each case. Brückner has more recently devised a furnace with several cylinders one below the other in order to render the working continuous, but this modification does not seem to have come into general use, and of furnaces with rotating heating chambers, the White-Howell furnace seems to be in most general employment for the operation of chloridising roasting.

The Stetefeldt furnace also enables a high degree of chlorination to be attained, and in point of capacity and smallness of fuel consumption it is at least equal to the furnaces just considered. It is in use at a large number of works in the Western States, and consists of a shaft with two fireplaces for heating, one at each side, the ore to be roasted falling freely down the shaft, and the flames passing up it. Through an opening at the top of the shaft the waste gases with some finer portions of ore pass down an inclined flue, also heated by a fireplace at the lower end, into a chamber in which the flue-dust is collected. From this the waste gases pass through more dust chambers, and lastly into a chimney with a good draught.

The construction of the Stetefeldt furnace is shown in Fig. 487, where B is the shaft down which the ore mixed with salt is allowed to fall from the mechanical feeder z, shown in detail in Fig. 488: G, G are the two fireplaces for heating the shaft, and they receive their air supply through the ashpits x, x, the flames from them passing into the shaft through the passages O, O, whilst air passes into the shaft through the channels M, M. The air partly serves to give the roasting an oxidising character, and partly serves to completely burn any unburnt gases. Through the opening v at the top of the shaft the waste gases carrying fine particles of ore pass down the sloping shaft H, heated from below by the fireplace E, the products of combustion passing through the opening O' and air entering through M'. From y

the gases pass into the chamber D, and then through flue-dust chambers to the chimney, the draught through the furnace being regulated by an iron damper. The roasted ore collects partly in the hopper J at the lower part of the main shaft, and partly in the hopper-shaped receptacles in D; all these hoppers have sliding doors through which the roasted ore falls into waggons underneath. R and Q are openings

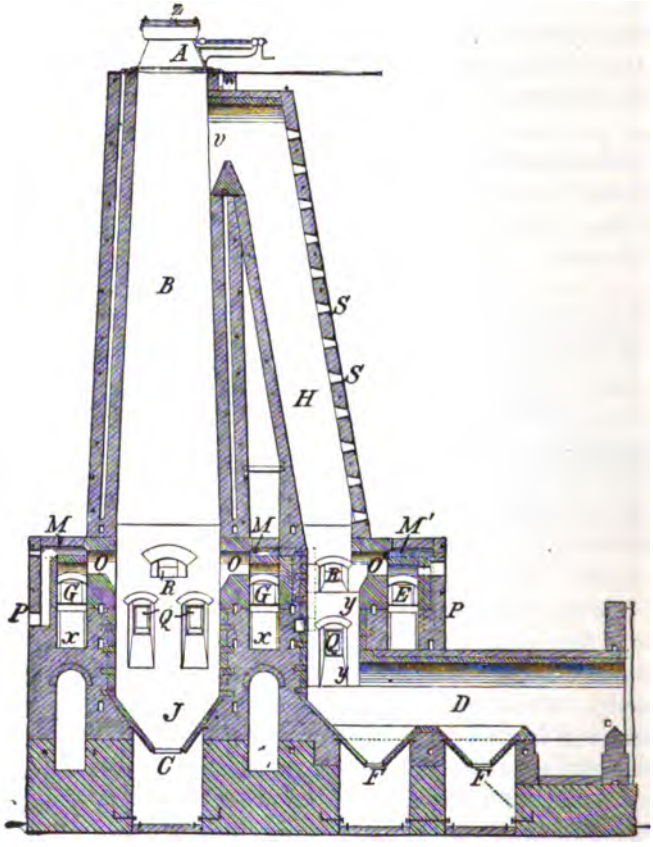


Fig. 487.

for clinkering and for admission of air, and the openings S, S similarly serve for removing any caked masses in the inclined shaft H.

The feeding apparatus is shown in Fig. 488, and consists of a perforated iron plate m, over which a screen of iron wire, n can be moved backwards and forwards. The perforated plate m rests on a cast-iron grate c, c, and the wire screen n forms the bottom of the frame E resting on the friction rollers G. The distance between the screens

m and *n* can be adjusted by moving the brackets *H*, on which the screen frame *E* rests on friction rollers *G*. The bracket *K* carries an eccentric shaft which is connected with the shaft *M* which moves the frame *E*, and with it the sieve *n*, backwards and forwards; *o*, *o* are adjustable iron blades fastened to the sides of the frame and reaching nearly to the lower screen over which they distribute the ore evenly. Owing to the movement of the top sieve frame, the ore falls through on to the lower perforated plate, and through it into the shaft, the amount of ore charged in being regulated by the number of strokes per minute made by the frame (usually 20 to 60), and by the distance of the distributing blades *o* from the lower perforated plate.

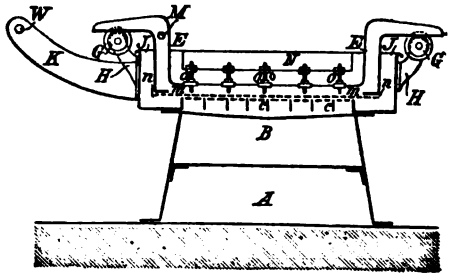


FIG. 488.

The height of the furnace shaft varies according to the nature of the ores and the amount to be worked in a given time, from 30 to 48 feet, and the furnace shaft, which is square in cross section, varies from 4 to 6 feet in the side.

The amount of ore which can be roasted in a Stetefeldt furnace depends upon the character of the material and particularly upon the nature of the impurities present in it. According to Egleston, the furnace at the Ontario Mill in Utah, visited by the author, roasts 55 tons of ore in 24 hours, that at the Northern Belle in Nevada, 55 to 70 tons, and at the Lexington Mill in Montana, also visited by the author, 30 tons of ores containing pyrites, blende and galena.

About half the roasted material collects at the bottom of the main shaft, and the other half in the flue-dust chamber (*D*), of which 80 per cent. will be found collected in the first hopper. The ore is drawn from the furnace and heaped together on cooling floors, where it is allowed to remain at least 12 hours for slow cooling and after-chlorination; the ore in the flue-dust chamber is allowed to stay there as long as possible because the after-chlorination proceeds quite well there.

The extent to which the silver in the ore is converted into chloride amounts to from 90 to 95 per cent., when the ore has been left for a sufficient length of time on the cooling floor. According to the statements of the managers of the Lexington Mill, Butte City, Montana, the ore is chloridised to the extent of 65 per cent. of its silver content.

immediately after reaching the bottom of the main shaft, whilst 2 hours afterwards, at the bottom of the main shaft, 75 to 80 per cent., and in the first flue dust chamber 72 to 78 per cent. of the silver content of the ore will exist as chloride. After 36 to 48 hours on the cooling floor the chloridising amounts to 92 to 93 per cent. of the silver in the ore. (Amalgamation extracts 94 per cent. of the silver content of the ore.)

The consumption of salt varies according to the nature of the ores from 3 to 18 per cent. of their weight, the amount required having to be ascertained by special experiment. At the Lexington Mill it amounts to 10 to 10·5 per cent. of the weight of the ore.

The consumption of fuel depends upon the character of the ores and the quantity roasted, the extreme limits being $1\frac{1}{2}$ and 5 cords of wood in 24 hours. According to Egleston, $2\frac{1}{2}$ to $2\frac{3}{4}$ cords of good dry wood are required to roast 20 to 25 tons of ore in 24 hours, and at the Lexington Mill at the time of the author's visit, 40 tons of ore were roasted in a Stetefeldt furnace in 24 hours with a consumption of $2\frac{1}{2}$ to 3 cords of wood. The furnace requires the labour of one man per shift for stoking and attending to the feeder, and of two men for emptying the furnace and attending to the cooling floors.

The furnace is adapted to ores of varying degrees of richness; at Reno they carry 30 to 800 ounces per ton, at Manhattan 100 ounces, at the Lexington Mill 40 to 60 ounces, at the Ontario Mill 60 to 100 ounces, and at the Northern Belle 30 to 100 ounces of silver.

According to the foregoing statements, it will be gathered that the Stetefeldt furnace is one of the best for the chloridising roasting of large quantities of silver ores and merits introduction into Europe. Concerning the selection of a particular furnace for the chloridising roasting of silver ores, the small furnace is practically now no longer used; where labour is cheap and well-trained, and only moderate quantities of ore are to be treated, the long-bedded calciner or the reverberatory furnace with multiple hearths may be used, and where wages are high, skilled labour not available, and large quantities of ore have to be treated, White or White-Howell and Stetefeldt furnaces are the most suitable.

3. Barrel Amalgamation Process

The barrel amalgamation process, also known as the European amalgamation process because it was devised and first used in Europe, is carried out in horizontal rotating barrels. After Born had introduced the chloridising roasting of silver ores into Vienna, and this process had been combined in 1786 at Schemnitz in Hungary

with the method of amalgamation in copper vessels (Cazo process), Gellert introduced the use of wooden vessels at Freiberg, and Ruprecht's later improvement was to mount the vessels horizontally and in such a way that they could be rotated.

The first amalgamating plant on a large scale with rotating barrels was erected in 1790 at the Halsbrücker Hütte near Freiberg, and thence it was introduced into many European works and into some in America. In Europe it has been superseded by smelting processes, and by wet processes in the strictest sense of the word, and in America by pan amalgamation, and at present is only in use in very few places, as at Arany-Idka in Hungary. It can be adapted, not merely to the working of ores, but also of metallurgical products such as matte, blister copper and speiss.[1]

The roasted ores, still containing an excess of salt, are first treated for some time with water and pieces of iron in the rotating barrels The salt dissolves in the water and the brine dissolves silver chloride, the iron reducing this to metallic silver, ferric chloride being at the same time reduced to ferrous chloride, and cupric chloride to the cuprous salt. Consequently ferric and cupric chlorides are not present to afterwards act injuriously in converting part of the mercury into mercurous chloride and causing a loss of mercury.

In the case of metallurgical products rich in copper in which large quantities of copper salts are always found after roasting, the metallic iron is replaced by copper, as if iron were used it would precipitate finely divided copper, which in this condition would be taken up by the mercury. Copper in lumps is only attacked by mercury to a slight extent. The silver set free is taken up by mercury, which is added some hours afterwards.

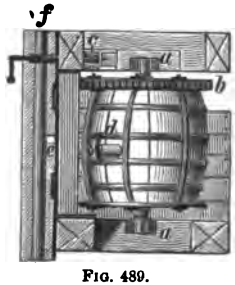


FIG. 489.

The arrangement of an amalgamating barrel is shown in Fig. 489. It consists of a barrel of oak or pine placed horizontally, and from 3 to 4 feet in diameter in the belly and 3 to 5 feet long, having an iron plate and gudgeon at either end. The gudgeons rest on bearings, and the barrel can be rotated by a toothed wheel at one end. For the sake of greater durability, as well as to secure a better admixture of the contents, the barrels are provided in their wide part with wooden plugs projecting internally. The filling and emptying of the barrel is effected through the open-

[1] K. Winkler, *Europäische Amalgamation der Silbererze*, Freiberg, 1848.

ing *d*, which can be closed with a wooden plug by means of a stirrup and screw.

An amalgamating plant with 4 barrels is shown in Figs. 490 and 491; *q*, *q* are the barrels (*quickfässer*) which can be rotated by the

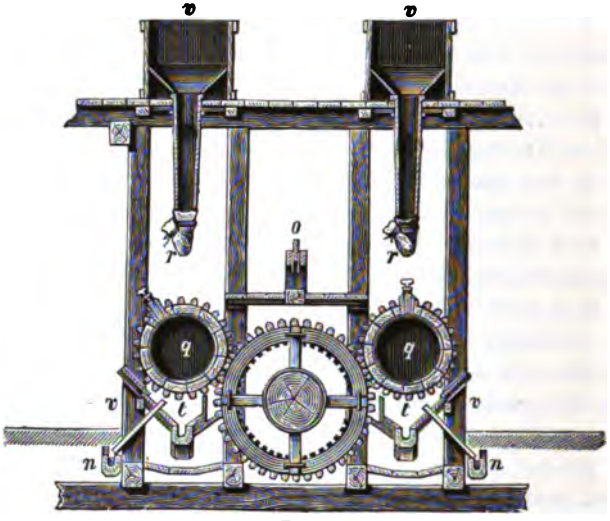


FIG. 490.

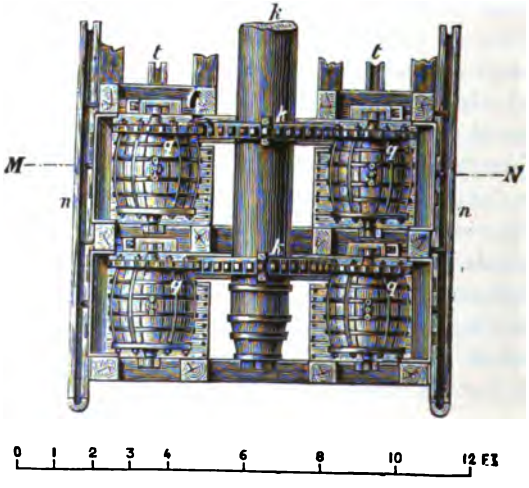


FIG. 491.

toothed wheels *k*, *k*; *v*, *v* are the charging hoppers with hose pipes at their lower ends for introducing the materials, *o* is a spout from which mercury is led into the barrels, which is provided with a plug hole

for each barrel, another spout leading from this to the plug hole of the barrel. The amalgam is run off into the trough *n* by the tube *v*, a hose pipe fastening it to the plug hole in the barrel.

About 3 cwt. of water are introduced into the barrel, 10 to 14 cwt. of finely-divided, roasted ore, and about 1 cwt. of iron in pieces about 1 inch cube, in the shape of cubes with rounded corners and edges; the barrel is thrown into gear with the driving axle and wheel and rotated for 2 hours at 10 to 12 revolutions per minute. During this time, as previously mentioned, the reduction of the silver to the metallic state occurs, and the reduction of ferric and cupric chlorides to ferrous and cuprous salts. Chlorides of cobalt, nickel, zinc and manganese are not attacked. The ore pulp in the barrel at the end of this time is of the consistency of honey and in the proper uniform condition for successful amalgamation. The barrel is now thrown out of gear, from 3 to 5 cwt. of mercury are added and it is again set in motion and allowed to run for 18 or 20 hours at the rate of 20 to 22 revolutions per minute. During this period the liberated silver is converted into amalgam and any remaining silver chloride is decomposed. Galvanic action between the mercury and iron is set up by the solution, the temperature rising to 30° C.

For the purpose of separating the amalgam from the residue, the barrel, which up to this time has been two-thirds full, is completely filled with water and rotated at the rate of 8 or 9 revolutions per minute for 2 hours. A small hose is then attached to an opening in the plug which had been closed up to now with an iron pin, and the amalgam is drawn off by the tube *v* into the trough *n*. From this it flows into an amalgam reservoir, and after the amalgam has been run off, the whole plug is withdrawn and the entire contents of the barrel are run off by means of the trough *t* into a vat, where the last portions of amalgam are separated by washing. The remaining liquor is run into settling tanks, evaporated and crystallised for Glauber's salts.

The amalgam obtained is washed in bowls or troughs and then pressed in canvas bags to separate the excess of mercury. If the amalgam is simply filtered, the mercury draining away only contains 0·06 per cent. of silver, whilst the mercury obtained on pressing the amalgam will contain 1·12 per cent. of silver. The amalgam produced at Freiberg by filtration through canvas contained 10 to 12 per cent. of silver and 4 to 6 per cent. of copper, lead and antimony.

The amalgam is retorted in cast-iron tubes or in a bell apparatus.

The loss of mercury in the barrel process of amalgamation is

small and amounts to 0·044 to 0·09 per cent. of the mercury used, or 22 to 45 per cent. of the silver obtained.

The loss of silver, including that incurred in roasting, retorting the amalgam and refining the bullion, amounts to from 5 to 10 per cent. of the silver content of the ore.

At Freiberg, ores containing from 0·09 to 0·26 per cent. of silver were roasted in charges of 5 cwt. with about 10 per cent. of salt, the operation being conducted in small double-hearthed reverberatory furnaces, and lasting 4 to 5 hours. The charge for the barrels was made up of ½ a ton of roasted ore, 3 cwt. of water, 1 cwt. of iron and 5 cwt. of mercury. The total loss of mercury in the process amounted to 0·044 per cent. of the quantity used, or 22 per cent. of the silver obtained.

At Arany-Idka in Hungary, where the process is still in operation, the ores, which consist chiefly of Jamesonite with 0·35 to 0·45 per cent. of silver, 1 to 2 per cent. of copper, 1·5 to 3 per cent. of lead, 0·3 to 0·5 per cent. of zinc, 10 to 14 per cent. of antimony, and a little gold, are roasted in a double-hearthed Hungarian furnace. The charge for the barrels is made up of 10 to 14 cwt. of roasted ore, 1 cwt. of iron, 3 cwt. of water, and 2¾ cwt. of mercury. The loss of mercury amounts to 0·09 per cent. of the total weight used, and the residue contains only 0·004 per cent. of silver.

In America the process has only been used in a few instances, in Mexico, Nevada and Colorado.

At the Pelican Reduction Works, Georgetown, Colorado, ores containing lead with 0·5 per cent. of silver and 25 to 30 per cent. of zinc are dry stamped and roasted in batches of 34 cwt. for 10 to 12 hours in a Brückner calciner. After the lapse of this time salt is added to the amount of 6 to 10 per cent. of the weight of the ore, and the roasting continued for from 4 to 6 hours longer. The roasted mass is then sieved and the lumps crushed and re-roasted, and the fine portions are amalgamated in barrels 4 feet in diameter and 6 feet 6 inches long, in charges of 1 ton. Mercury is added to the extent of 10 per cent. of the weight of the ore and the amalgamation lasts for 18 hours, the mercury being added after the lapse of 2 hours from the beginning of the rotation. The loss of mercury is 1 lb. per ton of ore, and 90 per cent. of the silver is obtained.

Amalgamation of Copper Mattes[1]

From the year 1832 to 1849 the Mansfeld copper matte was treated by the amalgamation process at the Gottesbelohnungs Hütte at

[1] K. Winkler, *op. cit.*

Hettstadt. The process was introduced in place of the desilvering of black copper by liquation, and was in its turn superseded by the Augustin process. The characteristic of this process consisted in the chloridising of the silver being partially effected in the wet way.

The copper matte containing 0·25 per cent. of silver was stamped, ground and sieved. The finer portions were roasted in lots of 3 cwt. on the upper hearth of the Mansfeld reverberatory calciner and then desulphurised on the lower hearth, the silver being then chiefly in the metallic state and the copper as oxide.. The roasted matte was mixed with a solution of salt (8 per cent. of salt on the weight of the roasted ore) and 12 per cent. of lime to a thin mud, well dried and then ground. This operation (called *einsümpfen*) effected a partial chloridising of the silver, the copper and iron chlorides formed being decomposed by the lime with the production of hydrates of the metals.

The ground and dried pulp was then subjected to another roasting operation in the same furnace with the object of completing the chloridising of the silver, and the roasted mass was amalgamated in barrels. The liquors obtained, which were rich in common salt, arising partly from the mutual action of sodium sulphate and calcium chloride, were used again for the second stage of the process. The washed residue was smelted in a shaft furnace for blister copper.

The loss of silver in the process amounted to 11 or 12 per cent., the greater part of this remaining behind with the copper.

The Amalgamation of Black Copper

This process was formerly employed in Hungary, but at the Stefanshütte where it was until recently in use, it has been superseded by an electrolytic process.

In order to obtain the copper in a finely divided form, it was heated to redness, and either stamped into granules or pounded with wooden hammers as soon as it was heated to the pasty stage.

The powdered material was then ground and sieved, and the finer portions roasted with salt in a Hungarian reverberatory furnace, the silver being converted into chloride partly through the direct action of the common salt and partly by the agency of copper chloride whilst the sodium of the salt was converted into soda. Towards the conclusion of the process, the heat was increased in order to decompose any basic salts. The roasting operation could be accelerated by an addition of pyrites or ferrous sulphate. In this case the chemical reactions were those ordinarily involved in the roasting of metallic

sulphides, together with a reaction between the sulphates and the common salt and also an evolution of chlorine and hydrochloric acid from the common salt, owing to the action of sulphuric anhydride upon it.

The roasted material was amalgamated in revolving barrels, copper balls being used instead of pieces of iron, as otherwise finely divided metallic copper would be precipitated, and in this condition would be taken up by the mercury. In this way an amalgam rich in copper would be produced, which on heating would give rise to a bullion rich in copper; the use of copper balls prevents this, as copper in large pieces is only slightly taken up by mercury. The copper reduces silver from silver chloride, and reduces cupric and ferric chlorides to cuprous and ferrous salts.

At Stefanshütte at Kaschau, the crushed black copper was mixed with 10 per cent. of common salt and roasted in charges of $5\frac{1}{2}$ cwt. in a double-hearthed Hungarian reverberatory furnace, the charge remaining 10 hours on the upper hearth and 5 hours on the lower one. The roasted mass was then sieved and the finer portions treated in lots of 12 to 15 cwt. with 1 cwt. of copper balls, warm salt solution and some milk of lime, for two hours in amalgamating barrels. After this time 4 cwts. of mercury were added and the amalgamation kept up for 18 hours.[1]

A similar process was in use at Schmöllnitz, working with black copper containing 0·37 to 0·5 per cent. of silver, the amalgamation residue being washed and afterwards smelted for its copper.

Winkler gives the loss of silver at $3\frac{3}{4}$ per cent., of which $2\frac{1}{2}$ per cent. is due to silver remaining behind with the copper residues; the loss of mercury amounted to 0·1 per cent. of the weight of the black copper worked.

In the case of black copper free from lead and gold, the amalgamation process is superior to the method of *leading*, but if lead be present, it finds its way into the amalgam and the gold is incompletely extracted by the mercury.

The amalgamation process for black copper is now entirely superseded by wet methods, such as the Augustin process and sulphuric acid extraction, and electrolytic methods.

The Amalgamation of Speiss

For this treatment the speiss must be first roasted in order to eliminate the arsenic and antimony present, and then submitted to a chloridising roasting with an addition of salt and ferrous sulphate.

[1] Winkler, *op. cit.*

In the chloridising roasting the common salt converts the metallic silver as well as silver arseniate and antimoniate into chloride. Any basic arseniates of the base metals are also converted into chlorides, and the higher chlorides of copper and iron thus produced act in their turn as chloridising agents on the silver compounds.

Ferrous sulphate accelerates the operation, the sulphuric anhydride evolved from it liberating chlorine and hydrochloric acid from the salt, and the ferric chloride produced exerting its chloridising action upon the silver.

In the amalgamation of cupriferous speiss, copper is used in place of metallic iron.

The process of speiss amalgamation was formerly used at Oberschlema in Saxony, and at Stefanshütte in Upper Hungary. At Oberschlema,[1] the speiss containing cobalt and arsenic was first roasted, and the arsenical fumes condensed in *poison chambers*, and the roasted mass was powdered and sieved. The fine material was then roasted in charges of 4 to 4½ cwt. with the addition of 8 per cent. of salt and 2 per cent. of dehydrated ferrous sulphate, the roasted product sieved, and the finer portions amalgamated in rotating barrels with pieces of metallic iron. The larger pieces were crushed and again roasted with the addition of 2 per cent. of salt and 0·5 per cent. of ferrous sulphate.

At the Stefanshütte 7 to 9 cwt. of crushed antimonial speiss from the smelting of fahl-ore containing 27 per cent. of copper, 62 per cent. of antimony, 9 per cent. of iron, 1 to 2 per cent. of sulphur, and 0·2 to 0·28 per cent. of silver, were roasted at a low temperature for 5 hours in a Hungarian furnace. The roasted material was then riddled, crushed and sieved, and the fine material in charges of 7 cwt. was roasted together with limestone for 5 hours on the upper hearth of a Hungarian furnace, and then for a similar length of time on the lower hearth. On the lower hearth, coal was added to assist in the elimination of the antimony, and the roasting was continued for 4 hours after the addition of 7 per cent. of salt.

After the chloridising roasting, the mass was amalgamated in rotating barrels in quantities of 12 cwt. It was first treated for 5 hours with 2 per cent. of salt and 1 cwt. of copper balls and a little lime to neutralise any free acid; after this 4 cwt. of mercury were added, and the rotation of the barrels continued for 15 hours more. The residues after washing were worked up for copper matte. The loss of mercury amounted to 0·06 per cent. of the total quantity used,

[1] Winkler, *op. cit.*

the consumption of copper was 0·053 per cent. of the weight of the speiss and the yield of silver amounted to 97·7 per cent. of the quantity present.

4. Pan Amalgamation (*Reese-River Process*)

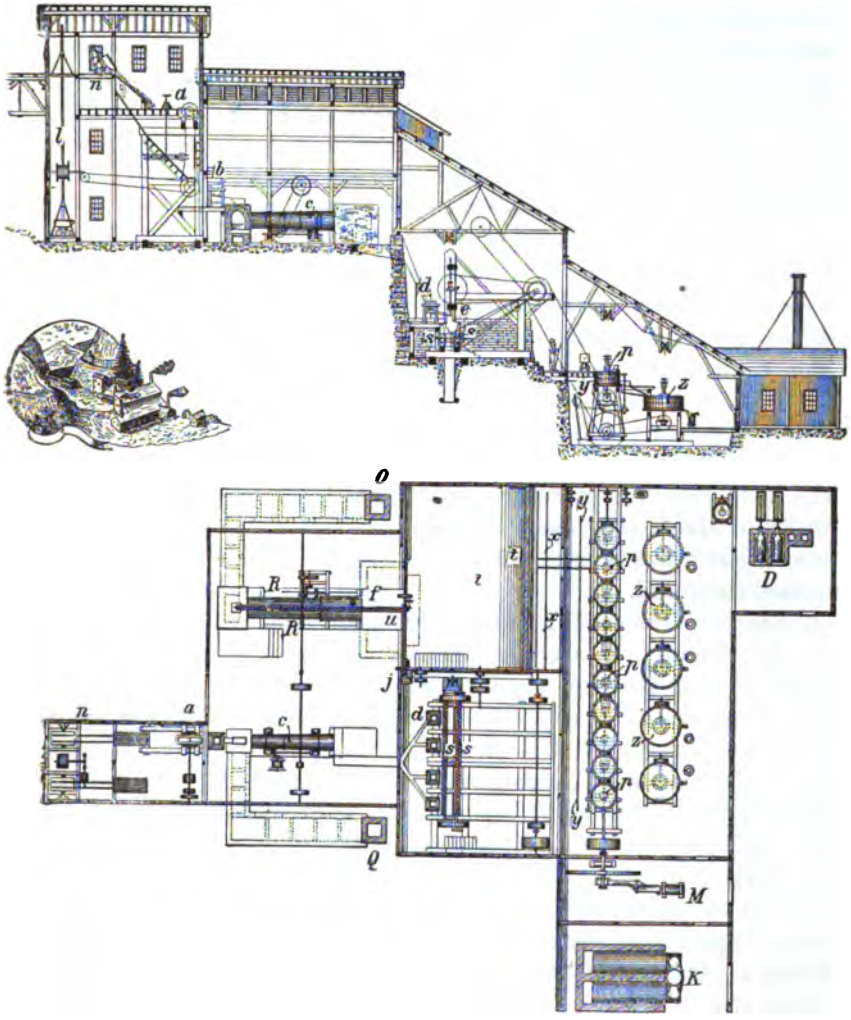
The pan amalgamation of roasted ores is carried out in pans which resemble in size and general arrangement those used in the Washoe process. The method of separating the amalgam from the residue, and the subsequent treatment of amalgam and residue being similar to the corresponding methods in the Washoe process, will not be considered again in detail. The yield of silver is higher than in the Washoe process, whilst the mercury losses are smaller, the silver yield reaching 97 per cent. whilst the mercury loss averages ¼ lb. on the ton of ore. The process was first used in the Reese-River district in Nevada, and receives its name from this circumstance; it is on the whole a quicker process than barrel amalgamation, and gives at least as good a yield of silver, and the loss of mercury is not any greater. Consequently, it is the process chiefly in use in the States for the amalgamation of ores that have been subjected to a chloridising roasting, and has superseded barrel amalgamation in even the few localities where it had been introduced.

The pans for the process are usually made of wood, as the sides of iron pans are quickly attacked by ores which have undergone a chloridising roasting. The roasted ores are generally put into the pan with water alone, without the addition of reagents, except in the case of very badly roasted ores, when salt and copper sulphate are added to decompose any silver sulphide present. After 1 or 2 hours the mercury is added, and during the whole process the mullers in the pan are so raised that no further grinding of the ore takes place, the only action of the muller being to bring the ore into intimate contact with the mercury.

The chemical reactions are similar to those of the barrel process, the chloride of silver being reduced to metal in the earlier stages of the process. The iron is partly derived from the wearing of the stamping machinery and partly comes from the mullers and the pans, the addition of iron borings being quite exceptionally necessary. The iron reduces the higher chlorides of copper and iron, and converts any mercurous chloride produced by the action of mercury on silver and other metallic chlorides to metal.

The chloridising roasting of the ores is chiefly conducted in rotating cylinder furnaces (Brückner, White, Howell) or in the Stetefeldt furnace.

The entire plant is usually arranged in terraces in order to avoid the lifting up of material as far as possible, and the arrangement of one of the newest plants erected in 1884 by Messrs. Fraser and Chalmers



FIGS. 492 and 493.

of Chicago, at the Granite Mountain Mill, Phillipsburg, Montana, is shown in Figs. 492 and 493. Similar plant is in use at the General Custer Mill, Vienna Mill and the Atlanta Mill in Idaho, with this difference, that at the three latter places, Brückner furnaces are used

for roasting instead of Howell furnaces, and the machinery at the Atlanta Mill is driven by water power.

The ore is carried up to the floor *n* by the lift *l* and emptied on to a grizzly. The material falling through passes to the feeder *b* of the drying apparatus *c*, which is of the rotating cylinder type. The larger pieces are crushed by the stone breaker *a*, and then go with the rest to the dryer. The ore from this is fed into the dry stamps *e* by means of the feeder *d*, and the stamped ore, delivered from both sides of the mortar, is carried by screw conveyors *s*, *s* to an elevator, which raises it to a hopper *j* over the roasting furnace. From this it is conveyed by screw conveyors to the White-Howell roasting furnace, and the roasted material discharged at *f* is left on the drying floor *t* to cool. From this it is conveyed by lines of rails *x* and *y* to the pans *p*, from which after the amalgamation it is run into the settlers *z*. *D* is the retorting plant for the amalgam. *K* and *M* are the boilers and engine, and *Q* and *O* are the chimneys of the drying and roasting furnaces.

All modern plants are arranged similarly, though the revolving drying and roasting furnaces may be replaced by Stetefeldt furnaces, the Lexington Mill at Butte City, Montana, one of the best arranged works of the kind, having furnaces of the latter type. The details of working at this mill, which was visited by the author in 1892, may be quoted as typical.

The ores worked at the Lexington Mill occur in veins in granite, having an average thickness of 4 feet. They are composed of a mixture of copper pyrites, iron pyrites, peacock copper, copper glance, a little fahl-ore, galena, zinc blende, mispickel, proustite, pyrargyrite, free silver and gold, with quartz, manganese carbonate and silicate, and smaller amounts of calcite and chalybite. In 1891 the average silver content was 0·0886 per cent. (28·5 ounces per ton) and the amount of gold 0·0018 per cent. (0·58 ounces per ton).

The ore is crushed by a stone breaker with jaws from 1½ to 2 inches apart and then freed from moisture in a Stetefeldt drying furnace. The salt is also dried in the Stetefeldt furnace, 20 tons of ore or 6 to 7 tons of salt being dried in 24 hours, and the ore is charged into the mortars of the stamp mills whilst still hot. The drying furnace has five terraces each 7 feet long and 5 feet 6 inches broad, and 98 cords of wood are used in drying 2450 tons of ore and 290 tons of salt; but in winter, when the purchased ore contains snow and ice, about 50 per cent. more fuel is required than in summer. The stamp mill consists of 60 stamps, 50 for crushing ore

and 10 for salt, and the mortars are of the double discharge type, the screens on the charging side being of brass wire gauze, and on the opposite side of perforated steel plate. They last from 15 to 40 days, and have 24 holes per linear inch. The stamps weigh half a ton, the height of fall is 8 inches, and the number of blows per minute is 92 to 95. The cams, tappets and stamp heads are of cast steel, the shoes of tough white iron, and the dies of hard, tough cast iron. These iron portions last from 3 to 4 months. The capacity of a stamp averaged 1·7 tons of ore per 24 hours in the year 1891. The salt is also stamped hot, but the stamps are lighter than those used for the ore, and the screens for the salt contain 400 meshes per square inch.

The crushed ore is mixed with 10 per cent. of salt and roasted in a Stetefeldt furnace 32½ feet in working height, square in cross section, and 4 feet wide in the narrowest part and 6 feet in the widest. Forty tons of ore are roasted in 24 hours with a consumption of 2½ to 3 cords of wood, and three men are required to attend to the furnace, two of them being occupied with the withdrawal of the ore from it.

The silver of the ore is chloridised in the furnace to the extent of at least 80 per cent., or 93 to 94 per cent. including the after-chloridising on the cooling floor. About 20 per cent. of the gold present is volatilised in the roasting operation. The ore remains from 36 to 48 hours on the cooling floor, in order to allow the after-chloridising to go on.

The ore is next put into the amalgamating pans, which have wooden sides, in quantities of 1½ tons. Water is added until the pulp has the consistency of thick mud, and the mullers are run for two hours. Mercury is now added to the extent of 10 per cent. of the weight of the ore, and the mullers are further run for 6 hours. The pulp is now diluted with water as previously described and run into the settlers. From the settlers it is run into an agitator and then run to waste. There are 20 pans, 10 settlers and 1 agitator. The amalgam is treated as described under the Washoe process.

The steam engine is of 180 horse power, and 9 tons of coal per 24 hours are required for the boilers.

The total loss of mercury amounts to 6½ to 8 ounces per ton of ore. The yield of silver reaches 97 per cent., the average for the year 1891 being 93·3 per cent., and the yield of gold which collects with the silver amounts to 60 per cent. The tailings in 1891 contained 1·94 ounces of silver, and 0·16 ounce of gold per ton. The quality of the amalgam is much deteriorated by the presence of lead, and if

the ores contain more than 5 per cent. of lead the process cannot be worked successfully.

At the Lexington Mill in 1891, 735,000 ounces of silver and 5767 ounces of gold were obtained.

5. Tina Amalgamation (*Francke-Tina Process*)

The Tina amalgamation, introduced into Bolivia by the German Consul Francke, consists in an amalgamation of roasted ore in wooden vats or *tinas* provided with copper bottoms and mullers with copper shoes. Portions of the pan walls are also covered with copper. The pan contents are heated by steam and the process differs from the Reese-River method in that copper is used in place of iron, and salt is added to the roasted ore in the *tinas*.

The chemical reactions are similar to those of the barrel process where copper balls are used, or to those of the Cazo process, the chloride of silver of the roasted ore dissolving in the salt solution and being reduced by metallic copper. The latter also reduces cupric and ferric chlorides to the cuprous and ferrous condition and prevents their acting on the mercury. Cuprous chloride dissolves in the common salt solution and reacts on the silver of the undecomposed ore as in the Kröhnke and Patio processes, the liberated silver being taken up by the mercury.

The Francke-Tina process is used at Huanchaca and Guadalupe, near Potosi, Bolivia, for refractory sulphur ores of silver. The construction of the *tina* used at Guadalupe is shown in Figs. 494 and 495. The *tina T* has wooden sides, the bottom consisting of a copper plate 3 inches thick and the height of the vessel is 5 feet. Its diameter varies, according to the weight of the charge, from 6 to 12 feet and on the sides are corrugated copper plates *K*. The muller *L* is furnished with copper shoes *S*, is rotated by the shaft and gearing *w*, and is adjustable as regards its distance from the pan bottom by the screw *v*. The amalgam and residue can be run off at the bottom through the opening *y*.

The ores are first dry stamped and then roasted in a small reverberatory furnace with two hearths, undergoing an oxidising roasting on the upper hearth and a chloridising roasting after the addition of 8 per cent. of salt on the lower hearth. From 2 to 2½ tons only are roasted in 24 hours.

At the beginning of the operation, the *tina* is filled with water to a depth of 12 inches, and salt is added in the proportion of 2½ to 3 cwt. for every ton of ore to be worked. Steam is now introduced, and

the muller set going at 45 revolutions per minute. As soon as the solution boils, which is the case after about half an hour, the ore is added, the usual charge being 2½ tons. After running for another half hour the first addition of mercury is made, followed by others at intervals, as is found necessary. The mercury is usually added in three equal portions, the weight of each depending on the nature of the ores; the second addition is usually made about the middle of the process (which lasts from 8 to 12 hours) and the last nearly at the



Fig. 494.

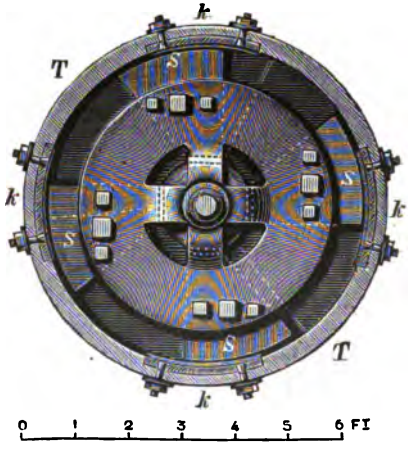


Fig. 495.

end. With ores containing 200 ounces of silver per ton, each mercury addition weighs 1 cwt., ores with 150 to 175 ounces receive ½ cwt. and ores with 20 to 30 ounces (0·06 to 0·09 per cent.) 44 lbs. of mercury, in each case for a charge of 2½ tons of ore. At the end of 8 or 12 hours the amalgamation is ended, and the *tina* is emptied in the same way as the pans. Each *tina* requires 2½ to 3 horse-power, or 1 horsepower per ton of ore.

The Francke process, which has quite recently been considerably

improved, can be highly recommended. It is at a disadvantage, however, as compared with the pan amalgamation, on account of its employing the dearer metal copper, where iron is used in the latter, but as the consumption of copper is not known to the author, a direct comparison of the two methods cannot be made.

1. Amalgamation with a Soluble Salt of Mercury

This method of amalgamation has not proved successful. The only process using this method which has been put into operation on the large scale was that of Designolle, which was used for some time at Schemnitz and Ravaspatak near Nagybanya in Hungary. In Designolle's process the mercury is reduced during the operation by the action of metallic iron upon a solution of mercuric chloride, and the mercury thus formed amalgamates more actively than if it were added as metal in the first instance. The essential features of the process may be best illustrated by the following experiment: If some small pieces of gold or silver are covered with a solution of mercuric chloride and metallic iron brought into contact with the precious metal, mercury will be precipitated on the latter and form an amalgam with it.

The process was carried out as follows: The ores (if they consist, as they do at Schemnitz and Ravaspatak, of silver sulphide and mixed sulphides) are first roasted with salt, and then treated in horizontal revolving cylinders of wrought iron with iron balls and mercuric chloride solution. The iron first precipitates gold and silver from solutions of their chlorides and then liberates mercury from the mercuric chloride, the mercury set free forming an amalgam with the precious metals. After this, mercury is added to the pulp to effect the union of the separate particles of amalgam, and the contents of the vessel are run into a settler, where the greater portion of the amalgam is collected. The ore pulp is then led over copper plates arranged one above the other in a fixed wrought-iron cylinder and lastly passed through two agitators.

The amalgam is freed from excess of mercury by squeezing in canvas bags and is then distilled in cast-iron tube retorts.

The mercuric chloride is prepared by treating the recovered mercury first with nitric acid and then with hydrochloric acid in earthenware vessels.

In Schemnitz and Ravaspatak, 90 per cent. of the silver in the ore was obtained, but only 60 per cent. of the gold. A considerable loss of mercury took place, as a portion of the mercuric chloride escaped decomposition and was run to waste with the residues, another

portion was converted into calomel and also lost, and a certain amount of mercury was always *floured*, and in that state could not be completely collected.

The Designolle process might give better results if roasting could be dispensed with, as in the chloridising roasting of ores containing gold a considerable loss is invariably experienced. The poisonous properties of mercuric chloride and the great loss of mercury also prevent the process from being successful. The author inspected the plant in 1886 at Schemnitz, and in 1887 the process was abandoned at Schemnitz and Ravaspatak, being replaced by a smelting or leading process.

2. The Recovery of Silver from Silver Amalgam

The amalgam, freed from its excess of mercury by filtration or more rarely by pressing, is next submitted to distillation. In this operation the mercury volatilises and is condensed, and the silver and base metals remain in the residue.

The vessels in which the distillation is conducted are either bells, upright or horizontal cylinders of cast iron, or glass retorts, the horizontal cylinder form having shown itself to be the most convenient, and being consequently chiefly employed.

The bell shape was formerly used in Europe, and is still in use in Mexico and South America. Vertical cylinders are used in Mexico, whilst in the United States the use of horizontal cast-iron cylinders is almost universal.

The arrangement of the old Mexican bell is shown in Figs. 496 and 497, *g* being a vessel provided with a depression *h*, through

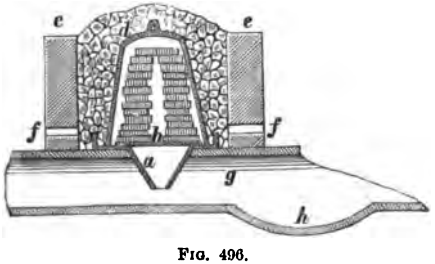


Fig. 496.

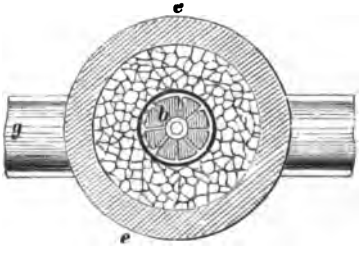


Fig. 497.

which water flows; *a* is a copper funnel with a rim, suspended in *g*, and *d* is a cast-iron bell (*capellina*) 3 feet high and 18 inches in diameter, usually suspended by chains, and which can rest on the rim of the copper funnel. On the funnel mouth a grate *b* is laid, and on this the amalgam is piled up, being made into slabs of such a shape

that six of them can be built into a circular ring. After the amalgam has been placed in position the bell is lowered and a circular wall of brick built round it with air-holes *f*, *f* at the bottom. In the annular space of about 8 inches broad, between the wall and the bell, charcoal is put and then ignited, and the distillation goes on for 15 hours. About 5 cwt. of charcoal are used in obtaining ¼ cwt. of silver.

At the present time in Mexico, vertical or horizontal cylindrical retorts have almost entirely replaced these bells.

The form of bell formerly used at Freiberg but afterwards replaced by horizontal cylindrical retorts is shown in Fig. 498; *a* is the cast-iron bell set in the vertical shaft *b*, beneath which is a vessel *d* filled with water, and containing a smaller vessel *e*. Resting on the bottom of the latter is a vertical bar *s* with foot *f*, carrying on its

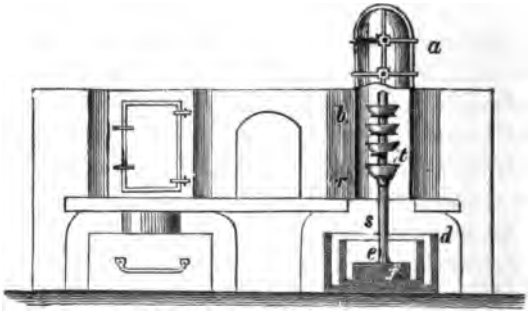


FIG. 498.

upper part a series of trays *t* for the reception of the amalgam. The space between the bell and the side walls of the shaft is filled with charcoal, and when the bell is heated the mercury condenses in the water vessel, whilst the silver remains behind on the trays. The charge of amalgam varied from 2 to 4 cwt.

In Mexico at the present time, vertical cylinders are principally used for retorting the amalgam obtained by the Patio process. They are made from mercury bottles with the bottoms removed; from 65 to 75 lbs. of amalgam are pressed into them, and they are then placed with the open end downwards on similar bottles with both ends removed, which are suspended in an iron plate, the amalgam being prevented from falling from the upper into the lower cylinder by an interposed perforated iron plate. The iron vessels are clay-washed, and the iron plate from which the lower ones are suspended, is covered with a layer of clay. The bottles are so arranged that the lower one stands in a trough of water and by heating the upper bottle

the mercury vapour passes through the holes in the iron plate and collects on the bottom of the water trough into which the lower bottle dips. The heating is effected either by charcoal or by the flames from a fire; in the first case a brick wall is built round the bottles, and the interspace between it and bottles is filled with charcoal; in the latter case, a permanent fire-grate is provided.

Figs. 499 and 500 show the arrangement of such a retorting plant with a separate fire-grate; *B* is the fire-place, *c* the fire-bridge, *D* the water vessel; *a* is the upper bottle, *d* the lower one, and *b* the iron plate from which the lower bottle is suspended. The heating chamber is covered with a movable lid; *e* is the flue, in front of which an iron cover, *f*, is placed during the retorting; *g* is a wall, forming the front side of the furnace, which is pulled down after the distillation. The distillation is finished when a wooden plate held

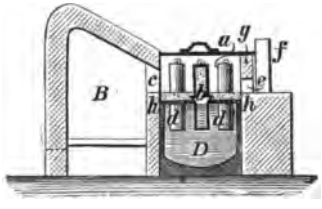


FIG. 499.

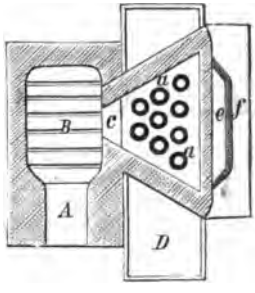


FIG. 500.

below the mouth of the lower flask is no longer covered with drops of mercury.

The distillation lasts 4 hours, and 2 cwt. of wood are consumed. The silver is refined in a small reverberatory furnace, and yields a bullion 990 to 998 fine.

Figs. 501, 502 and 503 show the arrangement of a distilling plant with horizontal cylindrical retorts in use in the United States. The cast-iron retorts are 12 to 14 inches in diameter, and 4 to 5 feet long, the walls being $1\frac{3}{4}$ inches thick. They are closed at the front end by a cast-iron plate, inserted through a special opening in the furnace wall. At the back the retorts narrow down to $2\frac{1}{2}$ inches in diameter, and are connected with a tube to carry away the mercury vapour. This tube passes through a cooling tank *D*, and the condensed mercury is led into a reservoir *E* also filled with water. The retorts lie wholly inside the furnace, their narrowed ends being supported by the brickwork of the furnace and their wider ends resting

on cast-iron bearers. At some places two cast-iron bearers are used, or worn-out stamp shafts from the mills are used in their place.

The amalgam, containing 1 part of silver to 5 or 7 of mercury, is either put into the retorts, in sheet iron trays fitting closely to the retort walls, or else it is charged in directly. The trays or the retorts, as the case may be, must be given a good coating of clay wash in order to prevent the silver sticking to them. The charge varies according to the size of the retort, from a quarter of a ton to a ton and the duration of the operation varies from 5 to 10 hours, $\frac{1}{3}$ to $\frac{1}{5}$

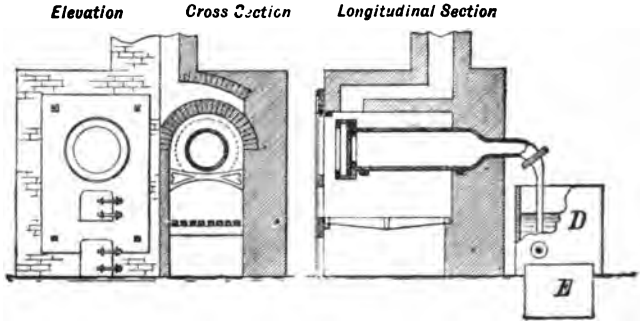


FIG. 501. FIG. 502.

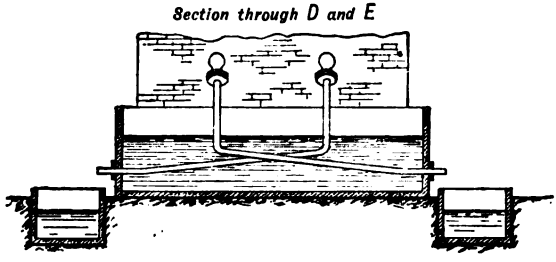


FIG. 503.

of a cord of wood being used for every $\frac{1}{2}$ ton of amalgam. The temperature is gradually raised to a cherry red, and at this temperature all the mercury down to 1 to $1\frac{1}{2}$ per cent. is distilled off. At higher temperatures the retorts would be blistered and distorted, and this quantity of mercury is accordingly sacrificed. Each retort lasts from 150 to 300 charges.

To hasten the distillation a partial vacuum has been made in the retorts at some works by the introduction of a steam jet into the condensing-tube. If the end of the condenser be connected with the front of the retort, then the last portions of the mercury may be removed, the air originally present in the retort keeping up a

circulation through retort and condenser and carrying with it the last portions of the mercury.

The silver obtained is generally refined in small reverberatory furnaces or, if tolerably pure, in crucibles.

3. The Production of Silver by Precipitation from Aqueous Solutions

In this method the silver contained in ores or metallurgical products is first converted into a compound soluble in water or certain aqueous solutions, and the silver is then precipitated as an insoluble compound by suitable reagents and the precipitate worked up for the metal.

The soluble silver compound is either the chloride which is soluble in salt or sodium thiosulphate solution, or else the sulphate which is soluble in hot water.

From the solution of silver chloride in brine, or from the silver sulphate solution, metallic silver is precipitated by means of copper, whilst from the thiosulphate solution the silver is precipitated as sulphide by sodium or calcium sulphide and the precipitate treated by dry methods. Occasionally the silver is precipitated from its solution in chlorides as iodide of silver.

The principal processes in which silver is obtained in solution in the form of chloride are the Augustin process, using brine as a solvent, the Patera process where sodium thiosulphate is used, and the Kiss process in which calcium thiosulphate is employed. With these must be associated the Russell process, where silver, not as chloride, but as metal or sulphide, is brought into solution by the agency of sodium-copper thiosulphate.

The method in which the silver is converted into sulphate and the latter dissolved in hot water is known as the Ziervogel process.

Processes in which Silver is obtained in Solution as Chloride

It is only in rare cases (as at Broken Hill) that the silver chloride in the ores is present to such an extent as to allow of their being directly treated with solvents, and it is as a rule necessary to convert the silver into chloride by a chloridising roasting. Endeavours to effect the chloridising of the silver in the wet way have not up to the present been successful.

As a solvent for silver chloride, sodium or calcium thiosulphate has proved most serviceable, as the solubility of silver chloride in aqueous solutions of these substances is greater than in salt solutions.

These solution processes are in certain cases preferable to either smelting or amalgamation methods, as for instance where the silver is present as a simple or mixed sulphide and the ores are either too rich in lead or zinc to be properly worked by the amalgamation method, or too poor in lead and too rich in zinc to be smelted with success.

The amalgamation process requires a more costly plant and a greater expenditure of power, but it has this advantage, that any native silver which may not have been converted into chloride, or any silver sulphide present, is taken up and amalgamated by the mercury. Though by the recent Russell process this particular objection is overcome, yet the method of obtaining metallic silver from the amalgam is a much simpler operation than the production of silver from its sulphide, in which condition it is obtained in the Russell process. These processes then are only indicated where amalgamation processes are inapplicable on account of the presence of too much zinc and lead. It is essential, however, that the ores shall not contain too much lead, arsenic and antimony, the lead being converted into chloride and sulphate in the roasting, both of which compounds coat the particles of ore and prevent the proper action of the solvents, antimony also forming easily fusible lumps. In addition, antimony and arsenic form arseniates and antimoniates of silver in the roasting operation, and these compounds are difficult to chloridise and are not so readily brought into solution by thiosulphate as is silver chloride.

The production of silver from cupriferous metallurgical products (black copper, copper matte, speiss,) by the Augustin process is now only rarely practised, having been definitely superseded by the Ziervogel process, extraction with sulphuric acid, or electrolytic methods.

The Augustin Process

In this process the silver in the ores or metallurgical products is converted into chloride by a chloridising roasting, and the chloride produced dissolved out by a solution of salt, the silver being afterwards precipitated from this solution by metallic copper.

The fact that silver chloride is soluble in concentrated salt solution was ascertained by Wetzlar. The mining juror Augustin, of Eisleben, introduced the process in the forties into the Mansfeld works for the extraction of silver from argentiferous copper matte in place of amalgamation. It was also introduced into Freiberg for the extraction of silver from copper mattes, but has long since been

abandoned at both places. At Mansfeld it has been replaced by the Ziervogel process and at Freiberg by the sulphuric acid extraction method. It is still in use at Kapnik, near Nagybanya, in Hungary, for ores, and is worked in combination with the Patera process. This combined process has recently been introduced into the Altai Mountains in Siberia (Bernaul). At Tajowa near Neusohl (Besterzebanya), Hungary, it was used up till 1893 for working argentiferous black copper. In the States it has never come into permanent operation.

At the ordinary temperature one part of silver chloride dissolves in 68 parts of a saturated salt solution. According to A. Vogel's researches (page 461) one litre of saturated salt solution dissolves 0·95 grams of silver chloride at the ordinary temperature, or 1·27 grams at 19·6°C. according to H. C. Hahn and W. M. Curtis. The solubility of silver-chloride in brine is far less than in solutions of calcium or magnesium chlorides. The solubility in brine is the same for all temperatures down to 6°C., but diminishes below this temperature.

Augustin's process, can consequently, on account of the comparatively slight solubility of silver chloride in brine, only be used for ores when worked in conjunction with the Patera process, and it should only quite exceptionally be used for working up metallurgical products.

With the object of extracting gold as well as silver, Röszner and Patera have suggested the use of brine saturated with chlorine, but this method has not come into use. The use of an after lixiviation with sodium or calcium thiosulphate has proved to be the best method for the extraction of the gold.

The roasting is carried out in reverberatory furnaces in a similar manner to the roasting which precedes amalgamation.

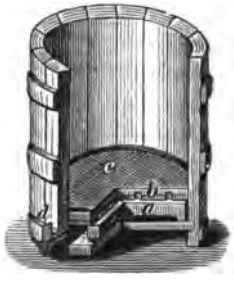


FIG. 504.

The dissolving of the silver chloride from the roasted material is effected in wooden vats with wooden gratings or perforated false bottoms, having a filter or layer of filtering material resting on them. The construction of such a vat formerly in use at Freiberg, is shown in Fig. 504. The false bottom *b*, made of perforated planks, rests on the wooden cross piece *a*, and over it is a layer of brushwood, on which is laid the filtering cloth kept in place by a wooden hoop fitting tightly to the sides of the vat. The material to be lixiviated is placed on the top of this, and the solution percolates through and runs out at the opening *d*.

Fig. 505 shows a vat used at Tajowa in Hungary for the extraction of argentiferous black copper which has undergone a chloridising roasting. On the false bottom a layer of birch twigs 1 inch deep is placed, and on this the cloth filter. A perforated float x distributes the liquid evenly over the material in the vat, which holds $2\frac{1}{2}$ cwt. of roasted material, and is provided with two exits v and w, the first rich liquor being run off through w, and the poorer liquid and the wash water through v. Below the vat is a board y by which any liquor, that may overflow, is conveyed into the trough n. From n the liquors flow into a precipitating vat.

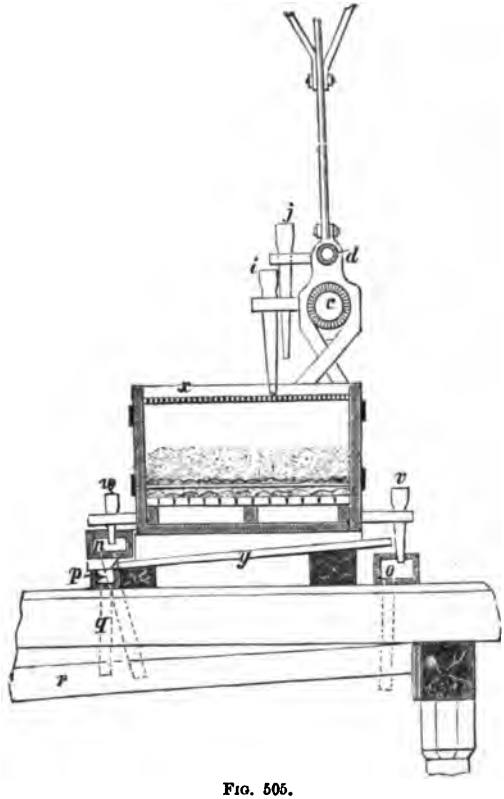


Fig. 505.

The more recent form of lixiviating vats used for the thiosulphate extraction in the United States is described below. They are considerably larger and hold as much as 50 tons of ore, the diameter varying from 10 to 15 feet and the depth from 3 to 6 feet.

After the roasted orehas cooled and has been sieved, it is put into these vats, which are generally arranged side by side on trestles, and then salt solution is run in. The salt solution is contained in a reservoir placed at a higher level than the vats, and can if necessary be heated by steam; it percolates through the material in the vats, dissolving out the silver chloride, and runs out from an exit pipe at the bottom into a spout, thence into a settling tank, and from this it flows into the precipitating vessel. The salt solution is allowed to flow through until a plate of copper placed in the liquor for a quarter of an hour, ceases to be coated with a bluish deposit of

metallic silver. The residue is then washed with hot water, and emptied out of the vats.

The precipitating vats are of similar construction to the lixiviating vessels, and several are usually placed in series, one below the other. The copper acts best when granulated, the smaller grained material being put into the upper vessel, and the larger pieces in the lower one.

A precipitation plant with three vats is shown in Fig. 506, the liquors flowing from the gutter *H* into the uppermost vessel, and

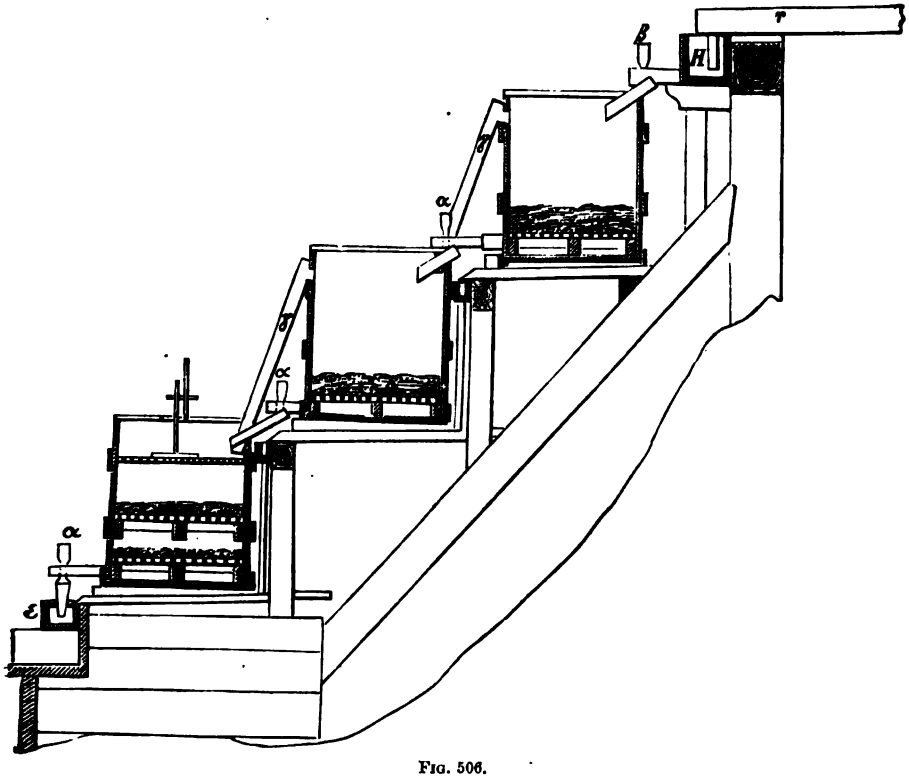


Fig. 506.

then through a tap into the second, and similarly into the third one. Each vat has also an overflow spout γ leading into the vessel below it, and the granulated copper rests on the wooden false bottoms, of which there are two in the lowest vat. From the bottom vat the liquor flows into a tank filled with scrap iron, in order to precipitate the copper. In the three precipitating vats there will be about 2 cwt. of copper, and in place of pure copper,

granulated argentiferous black copper may be used and its silver content thus obtained at the same time.

In the precipitation of the silver, cuprous chloride is produced which dissolves in the salt solution. If the liquors remain long in the tanks, some copper oxychloride is formed, which renders the precipitated silver impure. The silver forms a felt-like layer of small crystals on the copper, but if the liquor is too hot (over 70°C.) then the silver separates out in such a dense and finely-divided condition as to retard the progress of the filtration. This precipitated silver, which is known as *cement* silver, is rendered impure by the presence of basic copper and iron compounds, and particularly by lead chloride. From time to time it is removed from the copper, washed in a sieve with hot water to dissolve lead chloride, and then with hydrochloric acid to dissolve basic salts, and lastly melted in plumbago crucibles.

The liquors remaining after the precipitation of the copper are exposed to the air for a time, in order to separate the iron as a basic salt, and are then used again for extracting the silver chloride.

The Augustin process is applied to the extraction of silver from ores in combination with the Patera process at Kapnik, Nagybanya, Hungary, the ores after the chloridising roasting being first extracted with a salt solution, and then with a solution of sodium thiosulphate. By the use of this latter salt the greater part of the gold present is dissolved, as well as the last portions of the silver chloride. The same process is in use at Bernaul in the Altai.

At the time of the author's visit to Kapnik the process was being used for working pyritic slimes and selected ore. The slimes contained the gold in the native state, and the silver as sulphide. They contained 16 to 30 per cent. of zinc blende, 1½ per cent. of copper, 2 to 3 per cent. of lead, and 0·032 to 0·05 per cent. of auriferous silver, the silver carrying 0·8 to 1 per cent. of gold. Altogether the slimes contained about 70 per cent. of metallic sulphides. The selected ores were quartzose and free from lead, with 22 per cent. of sulphides, of which 10 per cent. was zinc blende, and contained from 0·05 to 0·07 per cent. of silver, the latter carrying 0·2 to 0·3 per cent. of gold.

The slimes and selected ores were mixed together in as nearly as possible equal proportions to form the roasting charge, dried over the flues of the roasting furnace, and then roasted in reverberatory furnaces with an admixture of 8 per cent. of common salt. The furnaces are shelf furnaces with four shelves lying one above the other, their general arrangement resembling that of the Malétra furnace, with this difference, that they are fired continuously by

means of a grate. When the charge reaches the third shelf, a further addition of salt to the extent of 4 per cent. is made. From 36 to 38 cwt. of ore can be roasted in this furnace in 24 hours. The roasted material is sieved to free it from lumps, which form 30 per cent. of its weight, and consist of incompletely roasted particles sintered together. These are crushed and re-roasted in a long-bedded calciner with the addition of 3 per cent. of salt, which is added half an hour after the charge has been placed in the furnace, the whole roasting operation lasting 6 hours.

The roasted ore from both furnaces is then lixiviated, the vessels in which this is carried out being wooden vats with false bottoms covered with a linen filter cloth. The roasted mass is placed on this in charges of $2\frac{1}{2}$ to 3 tons, and the first extraction is performed with a 22 to 25 per cent. solution of salt which has been heated to 80° C. by a steam coil. After this, an extraction lasting for two days with a cold aqueous solution of sodium thiosulphate of 3° to 5° B. takes place. By means of these two solutions 90 per cent. of the silver and 80 per cent. of the gold in the ores is obtained in solution, 60 per cent. of the silver being dissolved by the salt, and 30 per cent. together with the greater part of the gold by the thiosulphate. The residues have so far not been submitted to any further treatment.

From the salt solution the silver is precipitated by means of copper contained in two vats placed one below the other, the salt solution being heated to 28° C. by means of a steam coil. The copper which goes into solution in place of the silver, is precipitated from the liquors by means of metallic iron, and the liquors freed from silver and copper are settled and used over again for extracting fresh quantities of ore, being only finally rejected after three years' use.

The gold and silver are precipitated as sulphides by the addition of sodium sulphide to the thiosulphate liquors. The sodium sulphide is made by boiling flowers of sulphur with caustic soda in cast-iron vessels. The liquors from the precipitation process are used over again for lixiviation, any excess of sodium sulphide present being converted into thiosulphate by exposure to the air.

The precipitated cement silver as well as the precipitated gold and silver sulphides are put into a bath of molten lead in an iron pot, the lead having been previously heated to redness. In this way lead containing 0·6 per cent. of silver is obtained, and an argentiferous scum; the lead is cupelled and the scums are smelted in blast furnaces with other plumbiferous materials.

At Mansfeld and Freiberg, silver used formerly to be extracted from copper mattes by the Augustin process, but this has long ago

been replaced in Mansfeld by the Ziervogel process, and at Freiberg by the method of extraction with sulphuric acid.

In former years, at the works of the Boston and Colorado Smelting Company at Black Hawk, Colorado, copper mattes containing 25 ounces of silver per ton were roasted according to the Ziervogel method, and freed from the silver sulphate in them by extraction with hot water, and were afterwards roasted with salt and lixiviated with brine in order to obtain the remainder of the silver. This process is now abandoned, and at the company's works, which have been removed from Black Hawk to Argo, Denver, the mattes are smelted for fine metal and copper bottoms, and the fine metal is worked up by the Ziervogel process.

The Augustin process was applied for a time to the extraction of silver from speiss at the Stefanshütte in Upper Hungary, but was abandoned on account of the imperfect extraction it afforded. There was not only a considerable loss of silver owing to volatilisation, but large quantities of arseniate and antimoniate of silver were formed which were only imperfectly dissolved by the salt solution.

The Augustin process was in use up to the year 1893 for the production of silver from argentiferous blister copper at Tajowa, near Neusohl, in Upper Hungary. The method is now no longer used, as it is found to be more advantageous to employ electrolytic methods, or if the price of copper sulphate is high and sulphuric acid can be obtained cheaply, extraction by the latter is preferable.

One condition necessary for the successful working of black copper by the Augustin process is the absence in it of all but small quantities of antimony and lead.

At Tajowa, black copper with 80 to 84 per cent. of copper, 0·3 to 0·36 per cent. of silver and 3 to 7 per cent. of antimony was worked, as well as black copper from Schemnitz with 70 to 80 per cent. of copper, 0·2 to 0·25 per cent. of silver and 9 to 15 per cent. of lead.

The black copper was allowed to cool after tapping until it reached the pasty stage, and was then spread on an iron plate and broken up with wooden hammers. The mass was sieved and the fine material roasted. The pieces remaining on the sieve were sorted, the finer portions up to the size of linseed were ground, the coarser lumps stamped to powder, and the powdered material was then sieved afresh, the finer portions re-roasted and the coarser portions ground up fine.

The crushed black copper was so sorted that the lead content did not exceed 7 per cent., and the roasting was conducted in a Hungarian furnace with two hearths, the charge weighing 5 cwt.

The construction of the Hungarian reverberatory furnace is shown in Figs. 507–510, *a* being the lower, *b* the upper hearth and *c* the fire-place. The products of combustion pass over the lower hearth first,

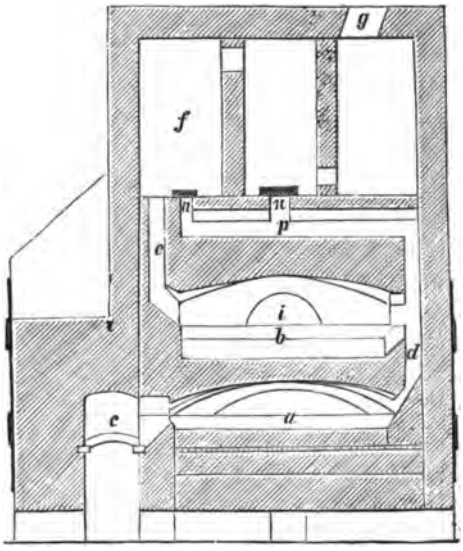


Fig. 507.

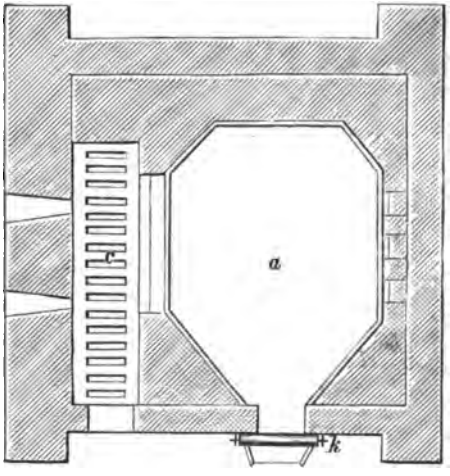


Fig. 508

then through the passage *d* and over the upper hearth, leaving the latter through the flue *e*, and passing through the flue dust chambers *f* into *g*, and away to the chimney; *i*, *i* are the working openings,

in front of which are rollers k, k to facilitate the working of the rabble. The ore after having been roasted for the proper time on the upper hearth is pushed through the passage h on to the lower

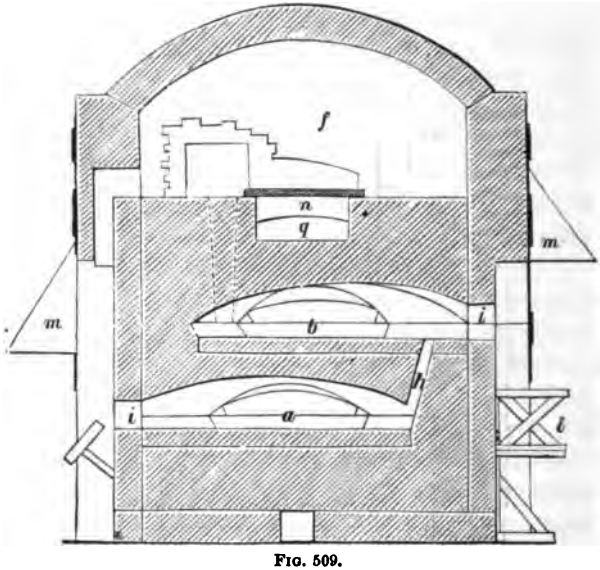


FIG. 509.

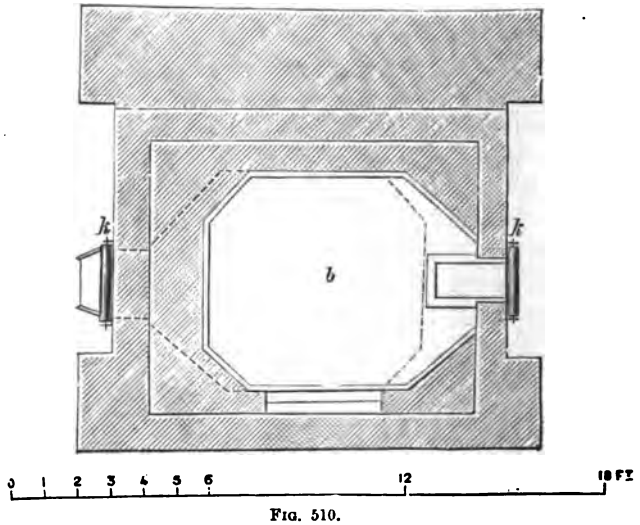


FIG. 510.

hearth, where the roasting is completed. The flue dust collecting in the chambers falls through passages n, n on to the floor p, whence it may be removed through q.

The material to be roasted was mixed with 15 per cent. of salt and put on the upper hearth, where it became red hot in an hour. It was kept thoroughly stirred, and after from 7 to 10 hours it was raked through on to the lower hearth, where it was heated and thoroughly rabbled with frequent additions of coal dust (up to 4 per cent.) to decompose any antimoniates present. The heat was then raised to bright redness and maintained at that point for a couple of hours in order to decompose basic salts. After this the firing was discontinued, the mass raked through for ½ to 1 hour, and then the after chloridising was allowed to go on in the furnace. Altogether the charge remained for 10 hours on the lower hearth.

The silver chloride was formed in the roasting, partly by the direct action of salt on metallic silver, soda being formed at the same time, and partly by the action of cupric chloride upon silver, cuprous chloride being produced.

The roasted material was sieved whilst hot, the fine portions being put into the lixiviating vats whilst still hot, and the coarser pieces ground up and added to a fresh roasting charge.

The charge for a lixiviating vat amounted to 1½ cwt., and the salt solution was used at a temperature of 10 to 15° C., as by using a cold solution considerably less chloride of lead and chloride of antimony are dissolved than with a hot solution. In this way the consumption of salt was diminished, and the precipitated silver obtained in a purer state, as these salts would partly separate out first. A hot salt solution also dissolves more cuprous chloride than a cold one, so that by using the latter the precipitated silver will contain less cuprous chloride and basic copper salts. During the extraction the salt solution was allowed to flow continually through the mass; the lixiviation was finished in 30 to 36 hours, and after that the residue was washed with hot water, and after washing contained only 0·005 to 0·01 per cent. of silver. It consisted chiefly of copper oxide and was smelted up for coarse copper.

The liquors containing the silver flowed along a trough into the precipitating vats shown in Fig. 506. The precipitated silver formed a felt-like layer of small crystals some 2 inches thick on the granulated copper used as a precipitant; this was removed periodically, washed in a sieve with hot water, or, if necessary, with hydrochloric acid to free it from basic salts, pressed, dried and melted in plumbago crucibles. The silver obtained was 982 fine.

The desilverised liquors traversed a long series of troughs containing scrap iron in order to precipitate the copper. The precipitated copper obtained still contained a little silver and was in

consequence submitted along with the black copper to a chloridising roasting.

The liquors freed from copper were used again for dissolving out silver chloride, but were previously freed from the lead chloride and iron salts they contained. The lead was precipitated by means of zinc, as the presence of lead chloride acts injuriously upon the solvent capacity of the liquor for silver, and the iron salts were deposited as insoluble basic compounds on allowing the liquors to stand for some time exposed to the air. The liquors together with the wash waters freed from copper were collected in a reservoir and pumped into another reservoir at a higher level, from which they ran into the vats. After being in use for 10 or 12 months they were run to waste.

The Patera Process

In this process the argentiferous ores first undergo a chloridising roasting, the silver chloride is then dissolved out by a solution of sodium thiosulphate, the silver precipitated as sulphide by the addition of sodium sulphide and the precipitated sulphide worked up for the metal. The precipitation of the silver by means of metallic copper is not feasible, as sodium thiosulphate solution dissolves both metallic silver and copper. Silver sulphide is, however, insoluble and the use of sodium sulphide as a precipitant also regenerates sodium thiosulphate. Sodium thiosulphate dissolves half its weight of silver chloride, whilst silver chloride requires 68 times its weight of common salt to dissolve it.

The use of thiosulphates as solvents for silver chloride was suggested by Hauch in 1846 and by Percy in 1850, but Patera was the first to introduce its employment on the large scale at the works at Joachimsthal in Bohemia in 1858. Kiss in 1860 introduced the use of calcium thiosulphate in place of the sodium salt at Schmöllnitz in Hungary, precipitating the silver as sulphide by means of calcium sulphide and in this way also regenerating the original solvent.

In both cases the thiosulphate solution decomposes the silver chloride and forms a soluble double salt, sodium-silver thiosulphate, or calcium-silver thiosulphate.

In Europe for a long time the Kiss process was given the preference over the Patera process because calcium thiosulphate and sulphide were cheaper than the corresponding sodium salts, and it was supposed that any metallic gold in the ore was only dissolved by the calcium salt and not by sodium thiosulphate. When, however, it was shown that the sodium salt dissolved gold as readily as the calcium one, both

processes came into use. In Europe, where most of the silver is produced by smelting with lead ores, neither of the processes are used to any extent, the only place where the Patera process is worked, in addition to the Joachimsthal works, being at Kapnik, Nagybanya, Hungary, where it is used in conjunction with the Augustin process. The Kiss process is still in use at some small private works near Nagybanya.

In the United States, the Patera process of extraction with thiosulphates was introduced in 1874 by Küstel at Melrose in California, and afterwards by O. Hofmann into several works in California, Nevada, and Arizona. At all these works it has been abandoned, but in Nevada, at the Bertrand Mill, where it was introduced in 1882, at the Mount Cory and the Cortez Mills, where it was started in 1883 and 1885 respectively, it is still in use.

It was introduced into Mexico in 1868 and is in use at several works.

In order to be available for treatment by the Patera process the ores must not be too rich in lead, copper or calcspar. In roasting, the lead is converted into chloride and sulphate, and both salts fuse in presence of silver chloride, and coat particles of undecomposed ore; they also go into solution with the silver, so that, in precipitating with sodium sulphide, lead sulphide is thrown down with the silver.

Copper also goes partly into solution (as sulphate and chloride) and is precipitated as sulphide with the silver, so that the presence of these two metals renders the silver sulphide precipitate very impure. Calcspar is partially converted into quicklime in roasting and the latter reduces silver from silver chloride, and diminishes the solubility of most silver compounds in the thiosulphate solution, lessening the tendency of silver to form soluble double salts. Caustic lime also precipitates any lead present as hydrate, and this coats the particles of silver chloride with an insoluble skin and prevents perfect lixiviation.

Up to a certain extent the injurious action of the lead and copper may be prevented by extracting the soluble salts with hot water before treatment with the thiosulphate solution. Russell also has discovered that lead may be precipitated as carbonate, insoluble in thiosulphate solution, by the addition of carbonate of soda. Copper is particularly injurious if it is present in the ores together with lead, because silver is more difficult to separate from a precipitate containing lead and copper sulphides than if only copper and silver sulphides were present.

Antimony and arsenic do not act as injuriously as in the Augustin process, because arseniate and antimoniate of silver give up their precious metal to thiosulphate solutions. Any metallic silver present

in the ores or produced during the roasting is also dissolved by thiosulphate solution, though undecomposed sulphide of silver, or its compounds with arsenic and antimony sulphides, is not attacked by thiosulphate.

It is only rarely that thiosulphate solutions are used to dissolve silver chloride existing already in the ore, and they are usually used for ores containing simple or compound sulphides of silver which have undergone a chloridising roasting. They have also been used in Mexico for the extraction of tailings from the amalgamation process.

The process is not used for the extraction of silver from metallurgical products.

The extraction of silver chloride existing already in the ore by means of sodium thiosulphate solutions is in use at Broken Hill, New South Wales. The ores containing lead carbonate, chloride and iodide of silver, embolite and native silver are first concentrated, and the tailings which contain a considerable amount of silver compounds, are extracted in the large American vats to be subsequently described, with sodium thiosulphate solution, which dissolves the chloride and a part of the iodide of silver. The silver is precipitated from the liquors with sodium sulphide, the precipitate dried, roasted in a small reverberatory furnace, and thrown into a lead bath.

As silver iodide only dissolves incompletely in thiosulphate solution, roasting the ores with salt in a Howell furnace has been recently introduced, and in this way not only is the iodide converted into chloride but any native silver is chloridised and the ores are rendered more spongy. From ores treated in this way and containing 20 ounces of silver per ton, 80 per cent. of the silver present is extracted with thiosulphate. The Howell furnace roasts 30 tons of ore in 24 hours.

A similar process is in use at Cerrogordo in Chili,[1] where the ores treated contain 0·1 per cent. of silver, mostly present as chloride and 0·0001 per cent. of gold. They are finely ground in ball mills and then roasted with 8 per cent. of salt in a Howell furnace. The Howell furnace is 27 feet long, 5 feet in diameter in the wider portion, and 4 feet 4 inches in the narrower part, with a lining 5 inches thick. From 35 to 38 tons of ore can be roasted in 24 hours, the furnace making from ½ to 1 revolution per minute. The roasting renders the chlorides spongy and partially chloridises any compounds of silver present. The roasted ore is extracted for 6 hours with a 1 per cent. solution of sodium thiosulphate, 60 to 80 per cent. of the silver content and 60 per cent. of the gold being obtained in solution. The

[1] Gmehling, *Oesterr. Zeitschr. für Berg.- und Hüttenwesen*, 1893, No. 37.

extraction is conducted in wooden vats 14½ feet long, 12 feet broad, and 3 feet deep, with false bottoms of wood covered with sacking.

The silver and gold are precipitated from the liquors as sulphides by an addition of sodium sulphide, the precipitating vats being wooden vessels of the same dimensions as the solution vats. The precipitated sulphides are sold to smelting works in Europe. Trials with the Russell solution (sodium-copper thiosulphate) have not given favourable results, but potassium cyanide solutions form very good solvents for the silver.

In order to obtain the silver from ores in which it is present as sulphide, or as sulphide mixed with arsenic and antimony sulphides, the crushed and dried ore is roasted with salt, the roasted ore extracted with a solution of sodium thiosulphate, and the silver precipitated as sulphide. The precipitated sulphide is dried and either put into a lead bath direct or after previous roasting.

At the smelting works in the United States[1] which possess the most recent and improved plant for the Patera process, the ores are treated in the same way as in the amalgamation by the Reese-River process, being crushed, dried, and then further broken up to the proper size by rolls or stamps. The plant is arranged in terraces to diminish the cost of conveyance from one apparatus to another. The ores are first emptied on to an inclined grid or *grizzly*, the larger pieces, that cannot fall through, passing on to the stone breaker and being added to the remainder after crushing. The crushed ore is dried either in revolving iron cylinders or in a Stetefeldt drying furnace and the dried ore is then finely crushed either in stamps or in rolls, Krom rolls having been found to give the best results in the States. The usual arrangement is to employ two sets of rolls, one below the other, the capacity of the two sets being from 35 to 40 tons in 24 hours. As to whether rolls or stamps are used depends upon the nature of the ore, rolls being used for preference if the nature of the ores allows it. Certain ores, however, particularly those containing large amounts of galena and zinc blende, require to be reduced to very fine powder in order to get a complete chloridising, and this can only be done by using stamps. A few trials will soon show which method of crushing should be adopted. Californian dry stamps are always used when the use of stamps is indicated.

The chloridising roasting is carried out in the same way, and in

[1] Carl A. Stetefeldt, *The Lixiviation of Silver Ores with Hyposulphite Solutions, with Special Reference to the Russell Process*, New York, 1888. "Notes on the Hydro-Metallurgy of Silver," C. H. Aaron, *Eighth Ann. Rep. of the State Mineralogist*, Sacramento, 1888.

similar furnaces (reverberatory with fixed hearths, revolving cylinders, or Stetefeldt furnaces) as in the chloridising roasting which precedes the amalgamation process.

The Hofmann revolving cylinder furnace should be mentioned here. This has a fireplace and a flue at each end of the revolving cylinder, and the flues as well as the openings for the admission of air to the fires, have adjustable dampers. By this arrangement the direction of the flames can be reversed and an even heating of the material ensured. The arrangement of the furnace is shown in Figs. 511–513, where t, t are the fireplaces at the ends of the cylinder,

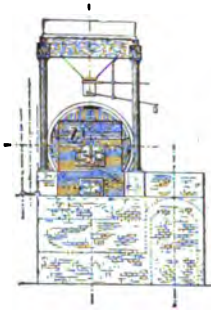


Fig. 511.

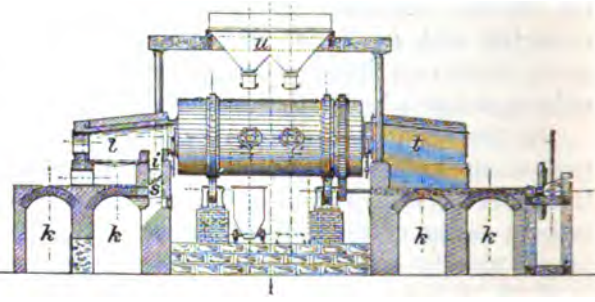


Fig. 512.

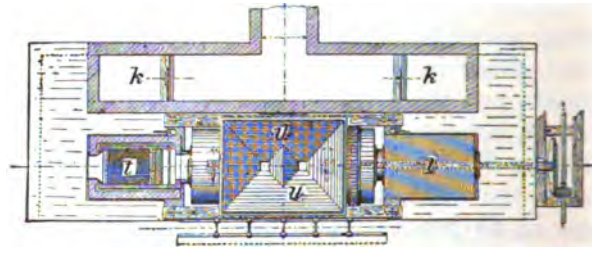


Fig. 513.

i, i the flues with dampers s, u the charging hopper, and k, k flue-dust chambers through which the waste gases pass on their way to the chimney.

Brückner furnaces, and more recently Stetefeldt furnaces in particular, are also used for the chloridising roasting. From 3 to 10 per cent. of salt is added according to the character of the ores, and to ores poor in sulphides some pyrites is added. With ores containing lead the temperature during the roasting is kept as low as possible in order to avoid the fusion of lead chloride and sulphate with the ore, and the formation of lead silicate. The lead must, as

far as possible, be converted into chloride, as this can be dissolved out with hot water, whilst lead sulphate cannot be so extracted.

At the Bertrand Mill, Nevada, Brückner furnaces 19 feet long and 7 feet diameter are used. They are rotated by the friction between the three sets of rotating wheels on which they rest and the iron friction rings that surround the cylinder. Each furnace holds 5 tons, requiring 10 hours for roasting, and 3 cords of wood are burnt for each furnace in 24 hours. The roasted mass is allowed to rest for 24 hours in order that the after-chloridising may take place. One man can attend to two cylinders during a shift.

The flue dust obtained also undergoes a chloridising roasting in a Brückner furnace.

The Stetefeldt furnace treats up to 70 tons of ore in 24 hours and may be recommended for use in the Patera process as it was for the amalgamation method.

The Extraction of Soluble Compounds of Base Metals by Means of Water

In the ores which have undergone a chloridising roasting, certain salts of the base metals will be found which are soluble in water, chiefly sulphates and chlorides of copper, iron and zinc, as well as lead chloride. These must be got rid of before extracting with sodium thiosulphate, otherwise the metals will be thrown down as sulphides in the subsequent precipitation of the silver, and in this way will contaminate the silver.

The roasted material is consequently extracted with water before being treated with thiosulphate solution, both operations being conducted in the same vessel, the freshly roasted material being charged in and only discharged after the extraction of the silver. If the Russell process is being used, the after extraction with sodium-copper thiosulphate is carried out in the same vessel.

The vats in which the operation is carried out are generally wooden vessels with false bottoms, cement tanks being occasionally used. The construction of these vats has undergone considerable alterations in America in recent times, large vats holding 50 tons being used in place of the small 10 ton vats formerly used, it having been found that the extraction can be carried on just as perfectly in the larger vessels. The diameter has been increased from 8 or 10 to 16½ feet and the depth from 3 to from 5 to 7 feet. The passage of the solution through the ore pulp can be hastened by the production of a vacuum by using a Körting's injector (Stetefeldt), this

arrangement allowing of the extracting liquid being continuously circulated through the layer of ore.

The details of a recent form of extraction vat worked in this way are shown in Figs. 514 to 517. The sides are of staves 3 inches

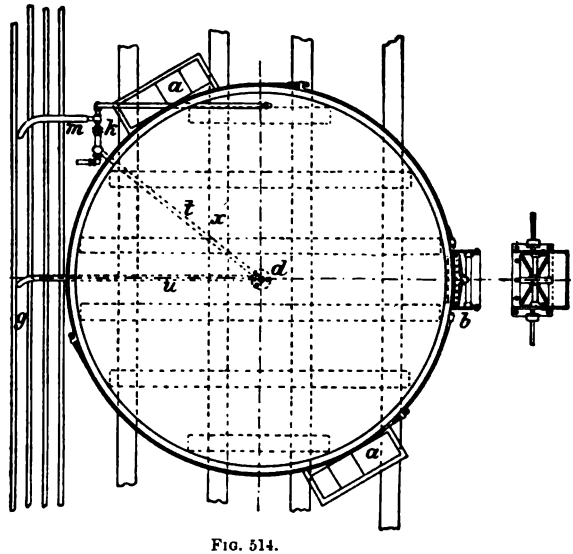


Fig. 514.

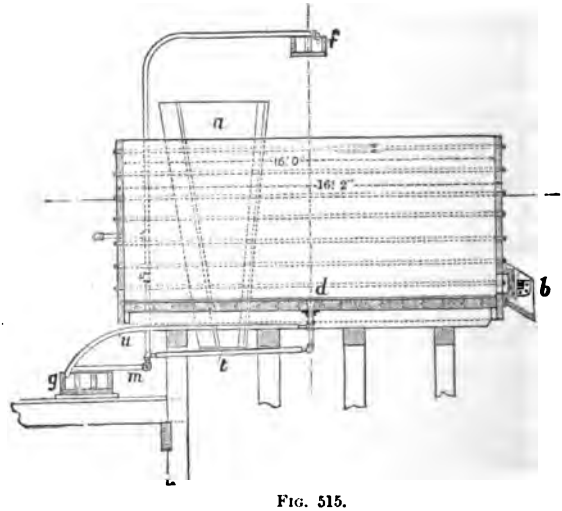


Fig. 515.

thick and the bottom is 4 inches thick, the joints being made with white lead, which is not attacked by thiosulphate solutions. The vessel is hooped with round iron $1\frac{1}{8}$ inches diameter, joined at

the ends as shown in Fig. 514. The bottom of the filter is covered with woven matting (*x*, Fig. 517) over which the filter proper of canvas is laid. These two layers rest on wooden laths (*z*, Fig. 516) 1·5 inches high and 1 inch broad, fixed to the bottom of the vat, 1 inch apart, by iron bolts set in white lead.

In order to allow of the circulation of the liquid at the bottom of the filter, pieces 3 inches broad and ½ inch wide are cut out of the wooden laths (*v*, *v*, Fig. 517), and the laths do not reach quite to the sides of the vat, an interval of 1½ inches being left. In this space the hoop *r*, *r* is laid, which is made of wooden laths 1½ inches high and 1 inch broad. In order to render all tight, a stout hemp rope is driven round at *s*. The woven matting covers the laths and the rim, whilst the canvas filter is made about 6 inches larger in

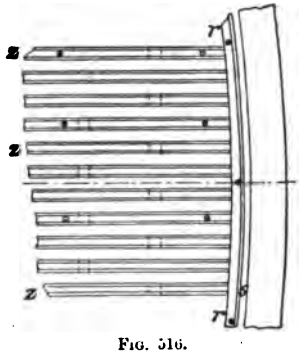


Fig. 516.

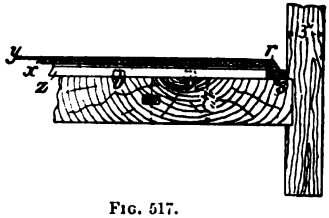


Fig. 517.

diameter than the vat, the projecting portion being pressed against the bottom and sides of the vessel by the rope *s*.

The ore to be extracted is brought along a line of rails running above the vat and tipped into it from the waggons. The lixiviating liquor is either run over the top from a spout or pipe, or else introduced from below through indiarubber hose, and the liquors are run off through an iron pipe in the centre of the bottom provided with indiarubber hose (*u* and *t*, Fig. 514), which can be clamped when it is necessary to stop the flow of liquid.

The liquors flow from *u* into the gutter *g*, and the pipe *t* is connected with a Körting's injector, by which a partial vacuum may be maintained in the space below the false bottom, and the filtration thus hastened. When using the injector the liquor may be either run into the trough *g*, or, by closing the tap *m*, may be forced up into the trough *f*, from which it is again run into the vat. The vat is either emptied by shovelling the residue into the spouts *a*, *a*, down which

it falls into waggons underneath, or it may be emptied through an opening reaching down to the filter, or by sluicing out the residue with water through the smaller opening *b*.

The vats are filled to such an extent that there is a space 12 inches deep from the upper edge to the surface of the ore.

If plenty of water is available and there is no danger of bringing silver chloride into solution, or if any silver chloride which is dissolved can be easily recovered without being contaminated with any great quantity of impurity, then the water is run on to the ore from above. If, however, water is scarce, and it is desired to collect any dissolved silver chloride in the vat itself, then the water is introduced below the filter, and rises up through the ore mass.

In the former case, the exit of the vat is closed and water run in until the vessel is full, the exit pipe is then opened and water allowed to flow through the mass until the liquid flowing away does not give any precipitate with sodium sulphide, indicating that all the soluble salts have been extracted.

When the water is introduced from below it is allowed to flow in until it covers the top of the layer of ore. It is then allowed to run back through the ore, and fresh water is simultaneously run in from the top until the soluble salts are washed out. In this way the dilution caused by the fresh water precipitates any chloride of silver and some of the lead chloride in solution in the brine, in the body of the ore mass, this acting as a filter. This method of extraction, though retaining the silver chloride which has been dissolved by the brine in the vat, has the disadvantage of also precipitating amongst the ore, lead, antimony and cuprous chloride if copper is present, so that the silver sulphide ultimately obtained will be contaminated with these metals. Stetefeldt prefers, therefore, to run in the water from the top, and to precipitate the silver in solution separately, only using the bottom method when very little water is available.

Cold water is best for washing, as hot water dissolves too much of the various chlorides and thus increases the amount of dissolved silver chloride. If the wash water only contains a little silver it is allowed to run to waste, otherwise it is precipitated by diluting the washings or by the addition of calcium or sodium sulphide. In the first method very large vessels are required, and the process is in consequence not to be recommended. The second method should be used if the water is alkaline from dissolved quicklime, as in this case only small quantities of base metals are precipitated, and a tolerably pure silver sulphide is thrown down.

If the washings contain copper, Stetefeldt recommends the use of

iron as a precipitant; this precipitates copper, which in its turn throws down the silver and goes into solution, only to be again precipitated by the excess of iron present.

The Lixiviation of the Silver with Sodium Thiosulphate Solution

After the treatment with water, sodium thiosulphate solution is run into the vat as soon as the water has sunk below the surface of the ore. This first forces the water out of the vat, and as soon as thiosulphate begins to run out, the solution is led into the precipitating vats.

Sodium thiosulphate has the formula $Na_2S_2O_3 + 5H_2O$ and it forms two double salts with silver, viz.:—

$$2\ Na_2S_2O_3,\ Ag_2S_2O_3 \text{ and } Na_2S_2O_3,\ Ag_2S_2O_3,$$

the first of these being more soluble in water than the second.

Sodium thiosulphate solution is only very slowly decomposed on exposure to the air, taking up oxygen and becoming converted into sodium sulphate.

The solution of chloride of silver in sodium thiosulphate solution generally proceeds according to the equation:—

$$2AgCl + 3Na_2S_2O_3 = Ag_2S_2O_3,\ 2Na_2S_2O_3 + 2NaCl,$$

one part by weight of crystallised thiosulphate ($Na_2S_2O_3 + 5H_2O$) dissolving 0·485 part of silver chloride, corresponding to 0·365 part of metallic silver.

Sodium thiosulphate solutions also dissolve metallic silver and gold, oxide, arseniate and antimoniate of silver as well as silver chloride. According to Russell's researches, 1 litre of sodium thiosulphate solution at the ordinary temperature dissolves 0·03 gram of metallic silver, and the solvent power is the same whether the solution contains 10, 25, 100, 150, 200 or 250 grams of the salt. Increase of temperature increases the solvent capacities of the solution, a solution containing from 50 to 100 grams of the salt dissolving 0·1 gram of silver at 54° C.

A litre of a similar solution dissolves 0·0002 gram of metallic gold, the gold forming a double salt of the formula:—

$$3Na_2S_2O_3,\ AuS_2O_3 + 4H_2O.$$

Silver oxide also dissolves with formation of a double salt:—

$$3Na_2S_2O_3 + Ag_2O + H_2O = 2Na_2S_2O_3,\ Ag_2S_2O_3 + 2NaHO,$$

one part of solid thiosulphate dissolving 0·2 of silver.

According to Russell, silver arseniate (Ag_3AsO_4), which dissolves best in warm solutions, is dissolved to the extent of 0·2 part of silver for 1 part of crystallised sodium thiosulphate. According to the same authority, silver antimoniate, which like the arseniate is dissolved more easily by warm solutions, requires 1 part of thiosulphate for the solution of every 0·05 part of silver in it. The solubility of arseniates and antimoniates is considerably lessened by the presence of caustic soda in the liquors.

Of the various other bodies present in the ores, copper is dissolved in very similar proportions to silver. Copper carbonate is also soluble, whilst the carbonates of lead, iron manganese, zinc and calcium are insoluble. Cuprous hydrate is soluble, but cupric hydrate and cupric oxide, as well as the oxides and hydrates of iron manganese and zinc, are not. Cupric chloride dissolves with the formation of a double salt.

Lead sulphate dissolves with the production of the double salt $2Na_2S_2O_3,PbS_2O_3$, its solubility varying with the strength and temperature of the solution.

Calcium sulphate dissolves, forming sodium sulphate and sodium-calcium thiosulphate, cold dilute solutions of sodium thiosulphate dissolving it more readily than hot and concentrated ones.

Quicklime is soluble, caustic soda and sodium-calcium thiosulphate being produced. It is soluble in thiosulphate solutions to the same extent as in pure water.

The solubility of silver chloride in sodium thiosulphate solutions is diminished by the presence of lead and sodium sulphates, and particularly by caustic alkalies and alkaline earths.

Lead sulphate forms the double salt previously mentioned, thus diminishing the amount of the solvent present.

Sodium sulphate does not diminish the solvent capacity of thiosulphate solutions for silver chloride to the same extent as caustic lime and caustic soda. A solution of sodium thiosulphate containing 1·5 per cent. of the crystallised salt had its solvent capacity reduced by 6 per cent. when 2 per cent. of sodium sulphate was present, or by 8 per cent. when 5 per cent. of sulphate was dissolved in it.

The presence of 0·5 per cent. of caustic soda in the thiosulphate liquor, according to Russell, diminishes its capacity for dissolving silver chloride by 30 per cent. and 0·5 per cent. of lime diminishes it by 11 to 24 per cent.

The injurious action of caustic alkalies and alkaline earths is due to their lessening the tendency of silver to form double salts, and in

the case of roasted ores containing lead they act injuriously by precipitating lead hydrate. In the chloridising roasting, any lead present is converted partly into chloride and partly into sulphate, and the greater part of the lead chloride is dissolved in the extraction with water, the lead sulphate remaining undissolved. Sodium thiosulphate solution dissolves both bodies, and if alkalies or alkaline earths are present they precipitate lead hydrate from this solution as a dense precipitate insoluble in thiosulphate which coats the particles of silver chloride and prevents its solution in the thiosulphate liquor. The presence of alkalies and alkaline earths may be due to the presence of calcium carbonate in the ores, which is partially converted into quicklime in the roasting, or to the sodium sulphide used for the precipitation of the silver containing an excess of caustic alkali, or to an excess of caustic lime having been used in precipitating the lead, or to the presence of metallic silver or oxygen compounds of silver in the ore, in which case caustic soda is formed during the lixiviation.

The solution of sodium thiosulphate is preferably used cold, as hot solutions not only decompose more rapidly, but also dissolve larger amounts of the salts of the base metals. In the case of rich ores the thiosulphate liquors contain not more than 2½ per cent. of the solid salt, and, with poor ores containing large quantities of base metals, not more than 1 per cent.

The solvent is allowed to percolate through the ore until silver can no longer be detected in the issuing liquors. Calcium sulphide precipitates base metals as well as silver from the thiosulphate solution, so that the production of a precipitate on the addition of this reagent is not a proof of the presence of silver in solution. Hofmann recommends that the precipitate be dissolved in nitric acid salt or hydrochloric acid being added to precipitate silver and lead chlorides, the precipitate being then boiled with water when lead chloride dissolves and silver chloride remains. If there is any residue, or if the liquid is milky, silver is still present in the ore. A better method is to assay the ore which is undergoing extraction and ascertain what amount of silver still remains in it.

The time necessary for the extraction depends upon the silver content of the ore and the amount of clayey material in it, which governs the rate of flow of the solvent liquid through the mass of ore. It varies from 6 to 30 hours for each vat. After extraction the mass is washed with water, the wash water being run, together with the liquor, into the precipitation tanks. The residues are usually worked down to 4 ounces of silver per ton.

The Precipitation of the Silver from the Thiosulphate Liquors

In addition to silver the thiosulphate liquors usually contain lead, copper, gold, antimony, arsenic and calcium. The other metals, such as zinc, iron, and manganese, are removed by washing with water. The lead in the liquors is chiefly present as sulphate, as the greater part of the chloride will have been removed in the washing with water.

If there is a large quantity of lead in the liquors, it is advisable to precipitate it as carbonate before precipitating the silver as sulphide. Sodium carbonate suggested by Russell as a precipitant for lead will not precipitate either copper or silver from thiosulphate solutions. Calcium however is precipitated as carbonate, so that this reagent cannot be used when calcium thiosulphate has been used as the solvent, or when calcium sulphide is to be employed for the precipitation of the silver. If the lead is not got rid of before precipitating the silver, it is thrown down with it as sulphide.

The precipitation of the silver in the liquors is effected by the addition of a solution of sodium sulphide, whereby silver sulphide is precipitated, and sodium thiosulphate regenerated according to the equation :—

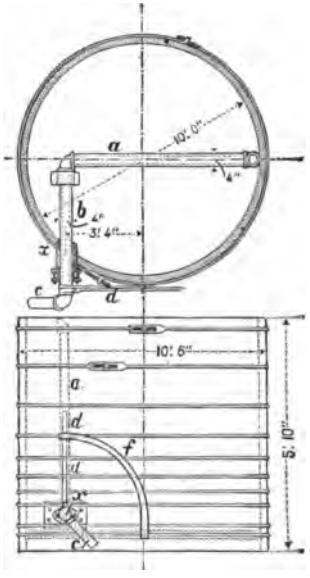
$$Ag_2S_2O_3,\ 2Na_2S_2O_3 + Na_2S = Ag_2S + 3Na_2S_2O_3.$$

Gold and copper and any salts of the heavy base metals are also precipitated with the silver. No more sodium sulphide should be used than is necessary to precipitate the metals, as the liquors are used over again for the extraction of fresh ore, and if they contain sodium sulphide some of the dissolved silver will be precipitated and in this way lost. Any sodium sulphide in the liquor must therefore be destroyed by the addition of fresh argentiferous thiosulphate liquors. Sodium sulphide may also be converted into thiosulphate by passing sulphur dioxide through the liquor, sulphur being precipitated at the same time.

The precipitating vats for these various operations—the precipitation of sulphides from the wash water, of lead carbonate from the liquors, or of silver sulphide from the same, are arranged similarly in each case. They are wooden vats about 10 feet in diameter and 8½ feet deep, and the contents can be stirred with wooden paddles during the precipitation, or mechanical agitators may be used. The liquor lying above the precipitate is drawn off after each precipitation by means of a movable elbow pipe inside the vat.

This is so arranged that the mouth can be gradually lowered in the vat, the liquor running off through a fixed pipe connected with it and terminating outside the vat. Instead of this arrangement, which is constructed of iron pipe coated with asphalte, an indiarubber hose pipe may be used, the end in the vat being raised or lowered, and the other end terminating outside the vat. The precipitated sulphides left after the liquors have been drawn off are sluiced out of the vat by a jet of water, being run off through an iron pipe coated with asphalte at the bottom of the vat.

Figs. 518 and 519 show the arrangement of a precipitating vat with exit pipe of iron *ab*, the arm *b* passing through a stuffing box *x* in the side of the vat, and being connected with the discharge pipe *c*. By means of the lever *d*, the elbow tube and the portion *a* can be moved through an angle of 90° from the vertical, so that the liquid can be drawn off from any depth, the pipe being fastened at the required angle by the lever *d* and quadrant *f*.



FIGS. 518 and 519.

If the lead is to be precipitated by soda before the sulphide of silver is thrown down, a duplicate vat similarly arranged must be provided.

In precipitating the silver, sodium sulphide is added whilst the liquor is constantly stirred, until a sample withdrawn from the vat gives only a very faint precipitate with sodium sulphide.

The precipitate is allowed to settle, the clear liquor drawn off as indicated above, fresh liquor allowed to run in, and the process repeated, the precipitate being only removed at intervals of several days or a week.

The sodium sulphide is made from caustic soda and sulphur. Caustic soda is dissolved in an equal weight of water in an iron pot, and powdered sulphur is thrown in little by little, the solution being heated to 80° C. The addition of sulphur causes the liquid to increase to twice or thrice its original bulk, so that at the beginning the pot must not be more than a quarter full. The sulphur dissolves in a few minutes, 100 parts of caustic soda requiring 66 of sulphur.

The sodium sulphide thus produced is run off in the liquid state,

and cast into moulds in which it solidifies, and it is either dissolved immediately or kept for subsequent use.

The amount of sodium sulphide used depends upon the amount of silver and base metals in the liquor, the average amounts at various works in the States being 1 to 1·25 parts of sulphur (and caustic soda in the above proportion) for every part of silver extracted.

The liquor, after precipitation of the sulphides, is used again for a further extraction, but as it has been diluted by the wash water, an addition of sodium thiosulphate is made to it to bring it up to the proper strength as well as to make up for the inevitable loss.

The total amount of thiosulphate used for the Patera process is very small, being in general between 2 and 4½ lbs. per ton of ore.

The Treatment of the Precipitated Silver Sulphide

The precipitate of metallic sulphides is generally sluiced out of the vats into a pressure vessel and freed from its adhering liquid by treatment in a filter press. It is then dried, but the temperature must not be allowed to rise to the point of ignition of the sulphides, and Stetefeldt has accordingly devised a drying chamber heated by the circulation of steam through iron pipes.

The dried sulphides are then roasted in a reverberatory or muffle furnace and brought into a red-hot lead bath contained in a cupellation furnace. They may also be charged into the bath of red-hot lead without previous roasting, the lead bath being either contained in a cupellation furnace or a reverberatory furnace, or in an iron pot as at Kapnik, Hungary. The product is either a rich lead which is cupelled, or *blicksilber* if the German cupellation hearth has been used.

The roasted sulphides have also been melted in plumbago crucibles with iron and borax, but in this way a matte is produced which contains a considerable amount of silver.

According to the nature of the ore, the Patera process extracts from 70 to 90 per cent. of its silver content.

The yield of silver is increased if the Patera process is combined with the Russell process, to be described later. Such a combination was being used when the author visited the Marsac Mill, near Park City, Utah (see description of the Russell process). The combination of this method with the Augustin process practised at Kapnik in Hungary has already been described on page 712.

The Kiss Process

In this process a solution of calcium thiosulphate is used for extracting the ores after a chloridising roasting, the silver being pre-

cipitated from the liquors by calcium sulphide, calcium thiosulphate being thus regenerated. This process is carried out in the same way as the Patera process, similar plant being used.

The solution of the silver chloride proceeds according to the equation :—

$$3CaS_2O_3 + 2AgCl = Ag_2Ca_2(S_2O_3)_3 + CaCl_2.$$

In this process any lead dissolved in the thiosulphate liquors cannot well be precipitated by sodium carbonate, as this would also throw down the lime; neither is an after extraction with sodium-copper thiosulphate (Russell's method) possible.

The solvent capacity of calcium thiosulphate for silver chloride is somewhat smaller than that of sodium thiosulphate, being, according to Russell, in the ratio of 91·5 : 100 for 1½ per cent. solutions.

Calcium thiosulphate solutions also decompose more rapidly than those of the sodium salt, taking up oxygen from the air and forming calcium sulphate.

The thiosulphate is produced by passing sulphur dioxide into solutions of calcium sulphide, the latter, (polysulphide), being made by dissolving powdered sulphur in lime water. For this purpose quicklime is dissolved in boiling water, and for every 1·5 parts of lime 1 part of crushed roll sulphur is added, the process being finished after 3 or 4 hours boiling, the reaction being :—

$$3CaO + 12S = 2CaS_5 + CaS_2O_3.$$

As a rule, the plant for the concentration of the liquors, the precipitation of the silver, and the working up of the silver precipitate is similar to that used in the Patera process.

The Patera process is on the whole preferable to the Kiss process, particularly as it allows of an after extraction of the material with sodium-copper thiosulphate solutions.

The Kiss process is in use at some works in the neighbourhood of Nagybanya in Hungary, in the United States, and in Mexico.

The Russell Process

In this process the silver present in the ore as simple sulphide, or in combination with arsenic and antimony sulphides, or as arseniate or antimoniate, as well as that present in the metallic state, together with any gold, is dissolved by a solution of sodium-copper thiosulphate. From this solution the silver is precipitated by sodium sulphide, and the sulphide precipitate worked up for metallic silver and copper sulphate. Calcium thiosulphate cannot

be used, as it is precipitated by sodium carbonate, and would be thrown down in the precipitation of the lead in the liquor by this reagent.

The process has not yet come into use for raw ores, though it is used at some American works as an auxiliary to the Patera process, the extraction with sodium thiosulphate being followed by an extraction with the sodium-copper salt, any silver or gold in the metallic state, or any sulphide, arseniate, or antimoniate of silver being dissolved by the latter substance. Silver chloride is not dissolved by sodium-copper thiosulphate.

There are several sodium-copper thiosulphates, and they are obtained by mixing solutions of sodium thiosulphate and copper sulphate; these double salts separate as yellow precipitates, when solutions, not too dilute, of the two salts are mixed. The salt obtained in this way by Lenz has the following formula:—

$$2Na_2S_2O_3,3Cu_2S_2O_3+5H_2O,$$

and is formed according to the equation:—

$$11Na_2S_2O_3+6CuSO_4=2Na_2S_2O_3,3Cu_2S_2O_3+6Na_2SO_4+3Na_2S_4O_6.$$

It is slightly soluble in water (1 in 352), easily soluble in sodium thiosulphate solutions, one part of the crystallised salt dissolving from 2·25 to 2·46 parts of the double salt according to the strength of the solution. This proportion corresponds very nearly to two equivalents of sodium thiosulphate and one equivalent of $2Na_2S_2O_3,3Cu_2S_2O_3+5H_2O$, and Russell therefore assumes that a double salt of the formula $4Na_2S_2O_3,3Cu_2S_2O_3+xH_2O$ exists in the solution. This easily soluble double salt is formed by mixing solutions of copper sulphate and sodium thiosulphate according to the equation:—

$$13Na_2S_2O_3+6CuSO_4=4Na_2S_2O_3,3Cu_2S_2O_3+6Na_2SO_4+3Na_2S_4O_6,$$

and it is a solution of this salt $4Na_2S_2O_3,3Cu_2S_2O_3+xH_2O$, which constitutes what is called the *extra* solution in the Russell process, as distinguished from the *ordinary* solution containing only sodium thiosulphate. It is prepared by dissolving together ¼ part by weight of sodium thiosulphate and 1 part of copper sulphate.

In presence of air the solution slowly decomposes with formation of sodium tetrathionate and separation of copper hydrate as follows:—

$$Cu_2S_2O_3+Na_2S_2O_3+2O+2H_2O=2Cu(OH)_2+Na_2S_4O_6.$$

In presence of sulphuric acid the precipitation of copper proceeds more slowly, the copper hydroxide dissolving in the acid until the latter is neutralised.

On heating to above 85° C. the salt decomposes, copper sulphide being deposited and sulphur dioxide evolved, and in presence of sulphuric acid this decomposition takes place at a lower temperature.

Caustic soda and quicklime precipitate cuprous hydrate from the solution, but this can be again dissolved by the addition of sodium thiosulphate. In presence of air the cuprous hydrate oxidises to cupric hydrate, which is insoluble in sodium thiosulphate solution.

At the ordinary temperature, sodium carbonate is without action on the solution, but if heated to over 30° C. a precipitate of copper carbonate is produced, which dissolves on the addition of more sodium thiosulphate solution. According to Gmelin this precipitate is cuprous hydrate.

A different sodium-copper thiosulphate, having the formula :—

$$8Na_2S_2O_3,3Cu_2S_2O_3+xH_2O$$

is obtained when 1 part by weight of crystallised copper sulphate is dissolved in water together with $4\frac{1}{2}$ parts of sodium thiosulphate. This salt is colourless and its aqueous solution decomposes less rapidly than that of the preceding salt. Free acids, however, decompose it tolerably quickly; caustic soda only produces a precipitate when heated to over 50° C., whilst sodium carbonate does not produce any precipitate.

Russell's researches disclosed the fact that solutions of the salt $4Na_2S_2O_3,3Cu_2S_2O_3+xH_2O$ had the property of quickly dissolving metallic silver, the solvent capacity of such solutions being at the ordinary temperature 9 times and at 50° C. $3\frac{1}{2}$ times as great as that of sodium thiosulphate solutions. The reason of this increased solvent power lies in the property of the copper salt of absorbing oxygen from the air and acting as a carrier of oxygen to other bodies (in this case to silver).

Metallic gold is dissolved only to the same extent that it is by sodium thiosulphate solutions.

Silver sulphide (Ag_2S) is quickly decomposed by the double salt, copper sulphide being precipitated and silver going into solution. For every 1 part by weight of Lenz's salt dissolved to saturation in sodium thiosulphate solution, 0·113 to 0·137 part of silver is dissolved from silver sulphide, the same amount of the salt in aqueous solution only dissolving 0·022 part of silver.

Sulphide of gold is also quickly decomposed, copper sulphide being thrown down and gold dissolved.

Arseniate and antimoniate of silver are decomposed in the same

way as by a simple sodium thiosulphate solution, and similar quantities of silver pass into solution.

The preparation of the ores, the roasting, washing out the soluble chlorides with water, the lixiviation with the solvent, and the precipitation of the lead with carbonate of soda are carried out in just the same way as the corresponding operations in the Patera process.

The sodium-copper thiosulphate liquor is not, however, regenerated, as the copper is precipitated with the silver on the addition of sodium sulphide. It must therefore be prepared afresh for each operation, and as it gradually decomposes when exposed to the air, it cannot well be kept in stock, but must be made immediately before use. This can either be done in a special tank placed over the leaching vat, or in the leaching vat containing the ore, by mixing the copper sulphate and sodium thiosulphate solutions in the proper proportion.

The composition of the liquor is varied according as to whether the ores are free from calcium carbonate or contain it; in the latter case caustic lime is produced in the roasting, and the liquors are then made to contain less copper.

A sodium thiosulphate solution containing 1½ per cent. of the salt is taken, and to this is added 0·6 to 1·2 per cent. of its weight of copper sulphate, if the ore is free from lime or contains arsenic acid in addition to lime, but only 0·13 to 0·33 per cent. of copper sulphate is added if the ores contain free lime. The liquor is used cold, or not hotter than 35° C.

The manner of extraction is also varied according as to whether the ores are free from alkalies or contain arsenic acid in addition to lime, or contain lime or other alkaline substances.

In the first case, the extraction with the extra solution of sodium-copper thiosulphate follows the extraction with sodium thiosulphate alone, the extra solution being continuously circulated through the mass of ore in the vat with the help of a Körting's injector. This lasts from 3 to 5 hours, and is continued as long as any silver is dissolved. After this a solution of sodium thiosulphate alone is run on for a second time, the degree of extraction being ascertained by assays of the residue.

In the case of roasted ores containing arsenic acid in addition to lime, they are treated first with the simple sodium salt as in the previous case, and then with the copper solution, with this difference: that the solution is not circulated through the mass, but simply allowed to remain on it for 10 to 12 hours. A washing with sodium thiosulphate solution is then given as before.

With ores containing lime, the extraction with sodium-copper thiosulphate precedes the extraction with the sodium salt, and the ore is washed with water between the two operations. The liquors are neutralised by the copper solution, and the injurious influence of the lime on the solution of the silver is thus diminished.

In order to avoid the effects of the dilution of the liquor by the washing, about a couple of pounds of copper sulphate dissolved in a little water are added to the wash water. The liquors are not circulated, but are allowed to remain in contact with the ore for 10 or 12 hours, an extraction with sodium thiosulphate solution concluding the operation as before.

From both the sodium and copper-sodium thiosulphate solutions the lead is then precipitated by the addition of carbonate of soda, and the liquors decanted from the precipitate are treated with sodium sulphide, which precipitates the copper and silver as sulphides.

According to Stetefeldt,[1] the following are the average results obtained in the precipitation:—

100 of caustic soda, converted into sodium sulphide, precipitate
162 parts of silver as Ag_2S.
155·2 „ „ lead as PbS.
94·5 „ „ copper as Cu_2S.
and 100 parts of Solvay soda precipitate.
191·4 parts of lead as carbonate.
36·9 „ „ lime „ „

The precipitate, consisting chiefly of silver and copper sulphides, is filter-pressed, dried and melted with metallic copper in cast-iron crucibles, forming argentiferous copper matte. The amount of copper added is such that the matte contains equal weights of copper and silver. The matte is powdered in ball mills, and roasted in a muffle furnace to convert the copper into oxide, and the roasted material containing the silver in the metallic state is treated with dilute sulphuric acid, the copper going into solution as sulphate and the silver remaining as such. The silver is washed, pressed into cakes, dried and melted in crucibles, the bullion being 950 fine.

The copper sulphate is crystallised out, and used over again to make fresh sodium-copper thiosulphate liquor.

The author saw this process in operation in 1892 at the Marsac Mill, Park City, Utah, U.S.A., and also met Stetefeldt there, one of the leading metallurgists of the day, and one who has rendered signal service in the introduction of the process.

[1] *Trans. of the American Inst. of Mining Engineers*, Cleveland Meeting, June 1891.

The ores which are worked there are partially oxidised, and contain 37 to 55 ounces of silver per ton, the silver being partly present as antimoniate. By means of the Patera-Russell process the ore is extracted down to 2·6 to 4 ounces of silver per ton.

The ores are dried in rotating cylinders, then stamped and submitted to a chloridising roasting in a Stetefeldt furnace, the best one for this operation when it is to be followed by extraction with thiosulphate solutions. After roasting, the ores are extracted in the vats previously described, first with water, to dissolve lead chloride and sodium sulphate, then with sodium thiosulphate, and, lastly, with sodium-copper thiosulphate solution.

From the solution and the washings the metals are thrown down as sulphides by the addition of sodium sulphide. From the sodium and copper-sodium thiosulphate solutions the lead is first precipitated with sodium carbonate, the lead carbonate precipitate being sold.

The solution decanted from the precipitated lead carbonate is treated with sodium sulphide, the precipitate thus formed containing from 40 to 43 per cent. of silver and 23 to 27 per cent. of copper. This is filter-pressed, and then melted in a cast-iron crucible with sufficient copper to ensure the resulting matte containing equal weights of silver and copper. The matte is powdered in a ball mill and roasted in a muffle furnace, and the roasted matte treated with dilute sulphuric acid in leaden vessels, the solution of the copper being assisted by the introduction of steam. The residual silver is separated from the copper sulphate solution by filtration through asbestos. The silver is washed with water, pressed into cakes, dried and melted in crucibles, a bullion 950 fine being obtained. The copper sulphate is crystallised out, and used for preparing fresh solution. The gases from the melting-pots and from the muffle furnace are forced by means of a Körting's injector through a solution of copper sulphate, in order to render them unobjectionable and to collect any silver carried over.[1]

Another method of working up the precipitate, which has only recently been introduced at the works of the Davey-Walter Refining Company, consists in treating it with hot concentrated sulphuric acid in cast-iron vessels. This dissolves both copper and silver, but leaves behind any gold that may be present. From the solution, which is run off from the residue into lead-lined wooden vats, the silver is precipitated; usually by means of copper, and the copper sulphate

[1] For further details regarding the treatment of the silver precipitate see *Trans. American Inst. Min. Engineers*, 1892, Pittsburgh Meeting; Stetefeldt, "The Marsac Refinery, Park City, Utah."

going into solution can be used for making fresh thiosulphate liquors. The author is not acquainted with the results obtained by this process.

The Production of Silver from Copper Ores which have undergone a Chloridising Roasting

In the extraction of cupriferous pyrites after they have been subjected to a chloridising roasting, by means of *end liquors*, that is by the liquors obtained in the precipitation of the copper by metallic iron, and consisting of chlorides of iron, copper and alkalies, the greater part of the silver in the roasted ore is obtained in the first liquor. From this the silver may be precipitated as iodide by means of an addition of iodide of potassium, sodium or zinc, or it may be precipitated as sulphide by sulphuretted hydrogen.

The first method is known as Claudet's process. The quantity of iodide which is necessary is greater than corresponds to the amount of silver present, as a part of the lead present is thrown down as lead iodide; cuprous chloride is also converted into cuprous iodide when zinc iodide is used. The precipitate consisting principally of silver and lead iodides and lead sulphate is reduced by metallic zinc in the presence of hydrochloric acid, metallic silver and zinc iodide being produced. The silver is obtained as a spongy mass mixed with pieces of zinc and containing 60–65 per cent. of lead (reduced from lead iodide), 5 to 6 per cent. of silver, and any gold that may have been present in the ores; the zinc iodide is used over again.

At Widnes near Liverpool from 1 ton of roasted ore, 178 grains of silver and 1½ grains of gold are obtained.

At Duisburg, Königshütte, Upper Silesia, Atvidaberg in Sweden, and formerly also at Oker, sodium iodide is used as the precipitant. The silver iodide precipitate is digested with sodium sulphide, sodium iodide and silver sulphide being produced, and the former is used over again for precipitation. The silver sulphide is treated by adding it to a lead bath. At Atvidaberg in Sweden the silver precipitate contains 10·5 per cent. of silver and 0·027 to 0·049 per cent. of gold. At Königshütte in Upper Silesia the precipitate contains 25 to 30 per cent. of silver and a considerable amount of gypsum.

Gibb introduced the use of sulphuretted hydrogen as a precipitant. By treating the liquors with this reagent nearly the whole of the silver is thrown down with the first portions of the copper sulphide precipitated. The sulphuretted hydrogen is prepared by acting with hydrochloric acid on Leblanc alkali waste, the gas being

forced by an air pump through an indiarubber pipe into the liquors. If copper is present in large excess no sulphuretted hydrogen escapes from the liquor. The precipitation is stopped when 6 per cent. of the copper present in the solution has been precipitated. The precipitate is filter-pressed and roasted in a reverberatory furnace, the copper being partly converted into sulphate and partly into oxide and oxychloride, whilst the silver is chiefly converted into chloride by the action of the chlorides remaining behind in the precipitate. The roasted mass is ground and treated in vats first with water and then with hot brine which dissolves the silver chloride. The solution is treated with milk of lime whereby all the heavy metals are precipitated. From the precipitate the copper is dissolved by dilute sulphuric acid leaving a residue containing all the silver as chloride. The residue contains about 9 per cent. of silver and 30 per cent. of lead.

Snelus proposes to blow finely divided iron through the liquid, the greater part of the silver and a proportionately small amount of copper being in this way precipitated.

The Ziervogel Process

This process was introduced in 1841 by Ziervogel at the Gottesbelohnungshütte, Hettstadt, of which works he was at that time manager, and it was there used for obtaining silver from the Mansfeld copper matte.

The process depends upon the fact that the silver in compounds of silver, copper and iron sulphides, may, if not present in too large an amount, be converted into silver sulphate by careful roasting. This silver sulphate is soluble in hot water, and from its aqueous solution the silver may be precipitated by metallic copper.

On carefully roasting copper matte containing not too great amounts of iron sulphide and silver, ferric sulphate is first formed in addition to iron and copper oxides, and as the temperature is raised this is decomposed and sulphuric anhydride is evolved. The latter as well as the oxygen of the air bring about the formation of copper sulphate, this latter salt being stable at a temperature at which ferric sulphate is decomposed.

On still further increasing the temperature, copper sulphate also decomposes into copper oxide and sulphur trioxide, or sulphur dioxide and oxygen. The sulphur trioxide acts by converting the hitherto undecomposed silver sulphide into sulphate, sulphur dioxide and oxygen being produced, the latter substance exerting a powerful

oxidising action upon the silver sulphide. Silver sulphate is stable at the temperature at which copper sulphate is decomposed, so that if the operation has been carefully carried out, the product consists of copper and iron oxides and silver sulphate.

If the temperature is too high, silver sulphate also decomposes, forming metallic silver, sulphur dioxide and oxygen, so that the silver escapes extraction in the subsequent lixiviation.

If the matte contains arsenic and antimony in any considerable quantity, arseniate and antimoniate of silver are formed in the roasting, and they, being insoluble in water, occasion a loss of silver. The presence of lead or antimony sulphides causes small sintered lumps (*sinterknoten*) to be produced in the process, so that the particles enclosed in them escape thorough roasting.

It follows then that the material to be treated by this process must be one containing copper, iron and silver sulphides, and free from any considerable amount of lead, arsenic and antimony compounds.

The silver sulphate produced in roasting is dissolved out by hot water, and as its solubility is increased by acidifying the water with sulphuric acid, this addition is usually made.

According to Rammelsberg 1 part of silver sulphate dissolves in

180	parts	of cold water.
88	„	„ boiling water.
180	„	„ cold sulphuric acid of 10° B.
30	„	„ boiling „ „ 10° B.
20	„	„ „ „ „ 20° B.
4	„	„ cold sulphuric acid of 60° B.
0·25	„	„ boiling sulphuric acid of 66° B.
35	„	„ acidified copper sulphate solution of 10° B.

If cuprous oxide is present in the roasted material, metallic silver is precipitated on extraction with water; the roasting must consequently be carried on in such a way that any cuprous oxide formed in the earlier stages of the process is afterwards completely converted into the cupric compound.

By the addition of sulphuric acid to the lixiviating liquor, any basic salts present are partially dissolved, and in addition ferric sulphate may be formed which is able to convert silver into sulphate, ferrous sulphate being produced at the same time.

The silver is precipitated from the silver sulphate solution by metallic copper, and from the copper solution, which, acidified with

sulphuric acid, is used again for the extraction of the roasted ore, the copper is precipitated by metallic iron.

Ziervogel's process is principally used for copper mattes free from arsenic, antimony and lead, and containing not too high a percentage of silver. In order to obtain a satisfactory yield of silver it is necessary to repeat the operation of roasting and lixiviating with the residues from the first lixiviation if much silver still remains in them. The residues contain sufficient basic salts to yield enough sulphur trioxide on roasting to convert the silver present into sulphate. The lixiviated residues may also be smelted after drying, with auriferous sulphides, producing auriferous copper bottoms and an argentiferous matte (Argo, Denver, Colorado), which latter can be submitted again to the process.

With careful work the yield of silver in the process may amount to 92 per cent. (as at Mansfeld).

Ores are not worked by the Ziervogel process as they never possess the requisite degree of purity. Speiss also is not adapted for treatment by this method, as in the roasting considerable amounts of silver arseniate and antimoniate are formed, and the conversion of these salts into sulphate is incomplete.

The silver contained in black copper can be converted into sulphate by roasting the finely-divided copper with ferrous sulphate or pyrites. In this way copper sulphate is produced, and as the temperature is increased in the roasting, sulphuric anhydride is evolved which converts the silver into sulphate. This method of obtaining silver from raw copper is not, however, used, as the electrolytic process or the extraction with sulphuric acid is preferable.

The Ziervogel process is in use at the Göttesbelohnungshütte, Hettstadt, for the Mansfeld argentiferous mattes; at Argo, Denver, Colorado, for argentiferous mattes from the works of the Boston and Colorado Smelting Company, and at Swansea (Hafod works) in Wales.

As previously mentioned (see Copper), the copper schist of the Mansfeld mines is first burnt to get rid of the bitumen, then smelted for copper matte (*rohstein*) in blast furnaces, roasted in kilns, and the roasted matte treated in reverberatory furnaces for fine metal (*spurstein*).

This *spurstein* forms the material which is submitted to the Ziervogel process. It contains 74 to 76 per cent. of copper, and 0·44 to 0·46 per cent. of silver, besides sulphur and iron. The silver in it is mainly present in the metallic state. According to Plattner, the ferrous sulphide (FeS) in the matte, dissolves silver with the

production of subsulphide (Fe_2S) and silver sulphide, but on cooling the reaction reverses. Hampe[1] finds that molten copper sulphide dissolves silver which separates out again as metal on cooling.

The *spurstein* is first powdered in a Brückner-Sachsenberg ball mill having a capacity of 14 to 16 tons in 24 hours and the powdered matte is then roasted. This consists of two distinct operations carried out in separate furnaces, the preliminary roasting and the final or dead roasting. After the first roasting the mass is again ground up in ball mills as it is impossible to avoid a partial sintering, and it is then submitted to the final roasting.

In the first roasting, copper and iron sulphides are decomposed, copper and iron oxides are produced, the ferric sulphate formed is decomposed and copper sulphate produced. The formation of cuprous oxide, which would precipitate silver in the lixiviation process, is avoided as far as possible by keeping an oxidising flame over the roasting mass. The formation of cuprous oxide cannot be entirely obviated owing to the action of sulphur dioxide upon copper oxide.

The furnaces in which the roasting is carried out are so-called bakers' furnaces ("*bäckeröfen*") in which the necessary heat is furnished exclusively by the combustion of the sulphur in the roasting material. When a fresh charge is put in, the furnace is still red-hot from the preceding operation, and contact with the red-hot bottom of the furnace soon raises the charge to its temperature of ignition, that is to the point at which the sulphur begins to oxidise and impart fresh heat to the material. The charge must be continually rabbled and stirred, this being formerly done by hand, but a mechanical arrangement is now in use. For this purpose there are four hearths placed one above the other, the two upper and the two lower hearths being connected and each constituting one furnace, so that the powdered matte always passes over two hearths, one below the other, being charged on to the upper hearth and withdrawn from the lower one. The hearths are nearly circular in plan. Through the centre of all four hearths of the two furnaces placed one below the other, a vertical iron shaft passes, provided with gearing on the upper portion outside the furnace by means of which it can be revolved. Two scrapers are fastened to this shaft for each individual hearth, and as they revolve, the material on the hearth is thoroughly turned over.

The charge for each hearth is about 1 ton, and the roasting lasts from 4 to 6 hours, a double furnace, such as the one described, roasting 10 tons of material in 24 hours.

[1] *Chemiker-Zeitung*, 1893, 17, No. 92.

The material withdrawn from this roaster contains ferric oxide, cuprous and cupric oxides, silver sulphide, and sulphates of various metals, but particularly of copper.

This is finely powdered in ball mills and then subjected to the final roasting. The object of this final roasting is to convert silver sulphide into sulphate and cuprous into cupric oxide.

The final roasting is done in reverberatory furnaces having two hearths placed terrace-wise one beside the other. The lower of these hearths lies nearest the fireplace. The furnace is fired by gas (Zahn's system) in order to avoid the reduction of cupric to cuprous oxide.

The mass is kept constantly stirred and the temperature is raised in order to decompose the copper sulphate and to convert the sulphide of silver into sulphate. As previously mentioned the silver sulphate is chiefly formed owing to the action of sulphur trioxide, arising from the decomposition of copper sulphate, upon the silver sulphide present. If a sample of the roasting mass treated in a saucer with a little water shows glittering scales of metallic silver, cuprous oxide is still present, precipitating silver from the sulphate in solution. The roasting is finished when on treatment of a sample with water the solution obtained is only coloured very faintly blue and yields a thick curdy precipitate of silver chloride on the addition of salt. The charge is then immediately withdrawn from the furnace. The amount of charge contained on each of the two terraces of the hearth is 0·4 ton, and the time taken in roasting 6 to 9 hours.

The roasted mass is first sieved to free it from lumps, and when cooled down to 60° or 70° C., is submitted to the lixiviation process.

The lixiviation is carried out in wooden vats with double bottoms, 2 feet high and 2 feet 3 inches wide. Over the perforated false bottom is a layer of woven willow twigs, and on this a linen filtering cloth. The roasted mass is put into the vat in charges of ½ a ton and first extracted with 13 to 20 gallons of water at a temperature of 70° to 80° C. After this it is treated with hot copper sulphate liquors which are obtained in precipitating the silver from its sulphate solution by metallic copper, and which have been previously rendered slightly acid by the addition of a little sulphuric acid. This treatment is continued until the addition of salt solution to the liquor does not yield any precipitate of silver chloride. Each charge requires 1½ to 2 hours for its leaching. The residues, which still contain 0·024 to 0·04 per cent. of silver, are dried and again roasted to convert the last portions of the silver into sulphate. This roasting takes place in the second roasting furnace previously described,

and does not last longer than the final roasting of the matte. The addition of a sulphur compound is not requisite as there is a sufficiency of basic salts left behind to furnish the sulphuric anhydride necessary to convert the silver or silver sulphide into sulphate.

The residue after roasting is extracted a second time and then smelted for copper, its silver content being reduced to 0·015 to 0·018 per cent.

The smelting is done by mixing it with 10 per cent. of coal, drying it and smelting it for refined copper in an English reverberatory furnace. The refined copper contains 0·022 to 0·025 per cent. of silver.

The argentiferous liquors from the lixiviating vats are freed from suspended matter by settling or filtration, and then brought into precipitating vats where the silver contained in them is precipitated by metallic copper. The vats are wooden vessels 2 feet 6 inches in diameter, and possess a false bottom and filtering arrangement like the lixiviating vats. On this 16½ to 22 lbs. of granulated copper and 3 cwts. of copper bars are placed. The vats are placed on a terrace at a lower level than the lixiviating vessels, and below the first row a second row is placed, the vessels of which can be used when the precipitated silver is being cleaned out of those in the first row. At intervals of 24 hours the silver is taken off from the copper by means of wooden shovels, and any silver deposited on the copper bars is rubbed off by the workmen, who are provided with leather gloves for this purpose.

The silver obtained, which is known as cement silver, is rendered impure by the presence of sulphates, of metallic copper and of gypsum, the latter being derived from the lime in the water and the ashes from the roasting furnaces. The precipitate is broken up with wooden pestles in wooden vessels and then washed in a vat provided with a filter, first with hot water and then with acid silver sulphate liquors, which dissolve any copper present, an equivalent amount of silver being precipitated. After the copper has been got rid of, the precipitate is treated in a separate vessel with hot water in order to dissolve the gypsum present.

The cement silver thus purified is pressed in a hydraulic press, the cakes obtained dried in a muffle furnace with a large number of separate compartments and then melted in plumbago crucibles. The silver produced is nearly pure.

The desilverised liquid obtained by the precipitation is acidified with sulphuric acid and used afresh for dissolving silver sulphate from the roasted matte. At intervals (usually once a year) the copper is precipitated from the liquors by metallic iron.

The yield of silver amounts to 92 per cent. of the quantity present in the matte.

The arrangement of the extraction and precipitation vessels is shown in Fig. 520; *a* is the lixiviating vat, and *c* and *e* are the precipitating vessels.

From the extraction vat the argentiferous liquors flow into a settling tank (*b*) provided with a partition reaching nearly to the top. The suspended impurities collect chiefly in that side of the vessel where the liquors first enter, the clear liquid flowing over the top of the partition into the other division, and thence into the precipitating vat *c*. From the latter the liquor flows into a trough *d*,

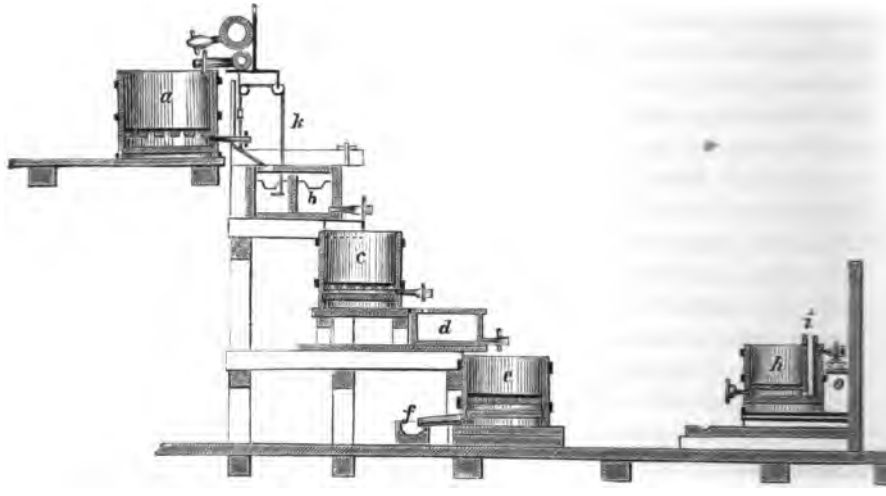


FIG. 520.

and can either be run directly into the next precipitating vat *e*, or, if the latter is having its silver removed from it, into a reservoir.

From the last precipitating vat the liquor flows along the spout *f* into a reservoir made of lead, where it is acidified with sulphuric acid, and is ready for extracting another charge of roasted ore.[1]

At the Boston and Colorado Smelting Works, Argo, Colorado, visited by the author in the spring of 1892, ores containing gold, silver and copper were smelted after roasting, to a copper matte containing 40 per cent. of copper, and 400 ounces of silver and 6 ounces of gold per ton. This matte was then roasted, and again smelted for

[1] The chemical changes in the roasting operation will be found dealt with in detail in the classical treatise of Steinbeck, *Preuss. Minist.-Zeitschrift*, vol. 11, p. 95.

concentrated matte with 60 per cent. of copper, 700 to 800 ounces of silver and 10 ounces of gold per ton. This was called white metal, and was roasted, ground, and then re-roasted, to obtain the silver in the form of sulphate. The silver sulphate was extracted with water and the silver precipitated by metallic copper, the copper being afterwards precipitated by metallic iron. The residue left after extraction, which still contained all the gold, was smelted for copper matte in an English reverberatory furnace, together with auriferous iron pyrites. The copper matte then underwent an oxidising *roasting* with the production of copper bottoms and argentiferous copper matte, which was again treated by the Ziervogel process. Before roasting, 2 per cent. of sodium sulphate is added, in order to ensure the conversion of all the silver into sulphate. The roasted mass is extracted by Ziervogel's method, and then sold to works that make copper sulphate and extract the gold and silver left after treating the leached matte with sulphuric acid.

The detailed treatment of the white metal is as follows. It is first roughly crushed so as to pass through a sieve of 6 meshes to the linear inch, and then roasted in a reverberatory furnace for 24 hours in order to free it from the greater portion of its sulphur content. The roasted material is then ground under edge runners (Chilian mills), so as to pass through a sieve of 60 meshes to the inch, and is roasted so as to convert its silver into sulphate. The roasting lasts 5 hours, the temperature being kept very low during the first $1\frac{1}{2}$ hours. At the end of the first hour and a half, the temperature of the mass will have attained to dull redness, owing to the combustion of the sulphur. At the end of the second period, which also lasts an hour and a half, the roasting mass has increased in volume in consequence of the formation of copper sulphate, the temperature also having slightly increased. During the third period, lasting one hour, the heat is raised in order to decompose the copper sulphate, and to form silver sulphate by the action of the liberated sulphuric anhydride upon any unaltered sulphide. In the fourth period, lasting for an hour, the temperature is maintained at the same point as in the third period, the charge being very thoroughly stirred in order to convert any cuprous oxide into cupric oxide.

Arsenic, antimony and bismuth form with the silver, compounds insoluble in water, and remain behind on the extraction of the roasted material. Bismuth is particularly injurious, as its sulphate mixes or combines with silver sulphate, and is not dissolved by water. On an average, the material after extraction retains about 40 ounces of

silver to the ton (0·1244 per cent.), the greater part of this being recovered by the after treatment of the residue.

The roasted material is extracted in wooden vats by means of hot water without any addition of sulphuric acid, and the liquors are run first through precipitating vats containing copper, in order to precipitate the silver, and then through vats containing scrap iron to precipitate the copper.

The precipitated silver is rendered impure owing to the presence of cuprous oxide and metallic copper, and in order to separate these bodies it is boiled for some time with water acidulated with sulphuric acid, air being blown in by means of a steam injector. The sulphuric acid in presence of air and water gradually converts the copper into sulphate, which dissolves. The silver is then washed, dried, melted and cast into bars, which have a fineness of 999 parts per thousand.

The material left after extraction still contains the whole of the gold content of the matte as well as 0·124 per cent. of silver, and 55 per cent. of copper as oxide. It contains in addition, ferric oxide, and lead and bismuth sulphates. It is smelted with auriferous pyrites, and with quartzose gold ores to a matte containing 10 to 15 ounces of gold per ton (0·0311 to 0·0467 per cent.), and 20 ounces of silver (0·0622 per cent.).

This matte, as previously mentioned, is submitted to an oxidising roasting in a reverberatory furnace, the products being an impure copper (copper bottoms), containing the gold and various impurities present in the matte, and an argentiferous rich matte, poor in gold and known as pimple metal or finished metal. The operation is precisely similar to the operation of making *best selected* copper in England, the preliminary oxidation, constituting the first part of the process, being carried out to such an extent that when the mass is subsequently melted, 1 part of copper bottoms is produced to every 15 parts of matte. The copper bottoms contain 100 to 200 ounces of gold, and 300 ounces of silver per ton; the greater the amount of foreign metals in them the more gold they can take up.

The composition of the bottoms varies according to the character and quantity of the impurities present in the matte, an analysis of one sample yielding the following figures:—

Copper . .	60·04 per cent.	Zinc . .	0·15 per cent.
Lead . . .	33·61 „	Gold . .	0·54 „
Arsenic . .	0·44 „	Silver .	1·35 „
Bismuth . .	0·40 „	Sulphur .	1·68 „
Iron . . .	0·08 „		

The matte or pimple metal contains in regular work 90 ounces of silver per ton (0·28 per cent.), and not more than 0·2 ounce of gold (0·0006 per cent.), together with 77 per cent. of copper.

This is desilverised by Ziervogel's process in the same way as the white metal, the residue from the operation consisting chiefly of copper oxide, and not containing more than 10 ounces of silver per ton (0·0311 per cent.). This, as previously mentioned, is sold and worked up for copper sulphate.

The method of extracting the gold from the copper bottoms is at present kept secret.

Formerly the lead was first liquated out from the copper in a reverberatory furnace; the latter then underwent an oxidising fusion, and after drawing off the slag the metal was granulated. The granules (containing 3 to 4 per cent. of gold and 2 per cent. of silver) were roasted in order to oxidise the copper, and then treated with dilute sulphuric acid in leaden vessels. The copper dissolved and left a slime of gold and silver behind. This slime, containing from 40 to 50 per cent. of gold, and 20 to 30 per cent. of silver, was melted in plumbago crucibles, and the bullion afterwards parted.

The Boston and Colorado Smelting Works before their transference to Argo, Denver, were situated at Black Hawk, Gilpin Co., Colorado. There the Ziervogel process was worked in conjunction with the Augustin process, the pimple metal, containing about 80 per cent. of copper, 20 per cent. of sulphur, 110 ounces of silver and 0·5 ounce of gold per ton, being first roasted according to Ziervogel's method, and extracted with water, then roasted with salt and extracted with brine. A detailed description of this method will be found in Egleston's book.[1]

The Extraction of Silver by Electro-metallurgical Processes

Electrolytic processes are only used for the extraction of silver from alloys in the wet way. The electrolysis of copper-silver alloys has already been dealt with in the article on copper, and the treatment of gold-silver alloys will be considered under gold, so that only the methods of obtaining silver electrolytically from lead-silver and zinc-silver alloys remain to be considered here.

Hampe has made some experiments upon the decomposition of argentiferous lead (work-lead) by electrolysis.[2] In these experi-

[1] *Metallurgy of Silver, Gold and Mercury in the United States*, 1887.

[2] *Zeitschrift für das Berg., Hütten-, u. Salinen-Wesen im Preussischen Staate*, 1882, p. 81.

ments the work-lead formed the anode, and the cathode consisted of sheet lead. Lead acetate solution was used as the electrolyte, and it contained 0·78 lb. of lead per gallon, and about 4 per cent. of glacial acetic acid. The current was furnished by two Meidinger-Pinkus balloon cells placed in series. In 456 hours, 1·5 lbs. of lead were precipitated, the current strength being 0·75 of an ampère and the surface exposed by the anode being 60·5 square inches, giving a current density of 1·8 ampères per square foot. The anode mud obtained weighed 11 grams.

The composition of the original work-lead, the deposited lead, and the anode mud is given in the following table:

	Work-lead.	Electrolytically-deposited lead.	Anode mud.
Lead	98·79767	99·99297	23·97
Bismuth	0·00376	0·00305	11·20
Copper	0·37108	0·0006	14·44
Antimony	0·55641	0·00099	29·7
Silver	0·254	—	18·435
Iron	0·00575	0·00041	traces
Nickel	0·0073	—	0·09
Zinc	0·00271	0·00198	1·8
Sulphur	0·00132	—	—

The working of this process on the large scale was suggested by Keith and was carried out at Rome in New York State. The work-lead was melted in a reverberatory furnace and cast into plates 2 feet long, 6 inches broad and $\frac{1}{8}$ inch thick, each weighing 9 pounds. These plates were enclosed in muslin bags and constituted the anodes. The electrolyte was a solution of lead sulphate in sodium acetate, and the current was furnished by a dynamo. The decomposing cells were cylindrical vessels 6 feet in diameter and 3 feet deep, and the cathodes were cylinders of sheet brass placed concentrically in the cells, the outer cylinder being nearly 6 feet in diameter and the inner one 2 feet, with a space of 2 inches between each cylinder.

The plates of work-lead were suspended in concentric circles to the number of 276 from the anode frame. This consisted of a copper hub with six radial arms, from which the lead anodes were suspended by means of brass plates and brass hooks. The anode frame was then lowered into the vat by means of a travelling crane in such a way that each lead plate hung between two brass cathodes.

The liquid serving as electrolyte was brought into the vat from below through a wooden pipe, and overflowed first into a reservoir, over the upper edge, and then into a pressure vessel, where it was

heated by a steam coil to 38° C. and forced again through the electrolysing vats. In this way the circulation of the electrolyte, one of the essentials for the success of the process, was secured.

The electric current passed through a pipe to the centre of the first vat, thence to the side of this vat and into the next vat, through which it passed in the same way. From this it passed successively through all the vats, of which there were 30. The current had an E.M.F. of 2½ to 3 volts and a strength of 1,000 ampères. The density of the current with an anode surface of 550 square feet was 20 ampères per square metre (10·76 square feet), and 9 lbs. of lead were deposited on the cathodes of each of the vats per hour, so that the deposition of 1 ton of lead required 10 days. The lead was deposited in a dendritic growth on the cathodes and grew towards the anodes. In order to prevent a metallic connection being thus made between anode and cathode, with the resulting short-circuiting of the current, the anode frame was arranged so that it could be rotated, and the lead crystals were removed by special scrapers and fell down to the bottom of the bath. The silver and gold remained behind in the muslin bags; the residue from these was melted with nitre in crucibles, and a button of the precious metals was thus obtained.

This method of separating lead from silver is inferior to the dry process of desilverising by means of zinc, and has, on this account, not come into further use. It must be borne in mind that the process of electrolytic separation is necessarily slow; that a previous melting of the work-lead is requisite, as well as a remelting of the lead which is deposited; that the working up of the mud containing the precious metals is difficult; that losses of liquor are unavoidable; and that the dilute liquors produced in washing the deposited lead require fuel for their concentration by evaporation.

The electrolysis of the zinc-silver alloy obtained in the desilverising of lead by means of zinc containing aluminium has been introduced in the present year (1894) at Hoboken, Antwerp, after the possibility of its employment had been proved by experiment. The products are metallic zinc, which is used over again for desilverising, and anode slimes which are worked up for silver (see page 564).

As far as present experience goes, electrolytic methods do not appear to possess any advantage over the other processes which are in use for the separation of zinc and silver from this alloy.

GOLD

Physical Properties

Gold possesses a characteristic yellow colour (golden yellow); this is lighter, the more silver it contains. When the gold is finely divided or in thin leaves, its colour changes to red, blue or green; thus the finely divided gold in ruby-glass or in purple of Cassius appears deep red, whilst thin leaves of gold are green by transmitted light.

Gold crystallises in the cubical system. Its fracture is hackly. It is softer than silver, but has almost the same tenacity as that metal. It is the most ductile of all metals; for example, Réaumur succeeded in producing a film of gold of a thickness of 0·00000218 millimetre (0·00000087 inch). Its ductility is greatly diminished by minute admixtures of other metals, especially of lead.

The specific gravity of gold is 19·30 to 19·33 at 17·4° C., after it has been fused and cast; according to G. Rose, 19·33 to 19·34 when it has been compressed, and 19·55 to 20·72 when it has been precipitated by ferrous sulphate.

Its melting point is given between 1,037° C. (Becquerel) and 1,240° C. (Riemsdyck). Violle found it to be 1,035° C. (in 1879).

At elevated temperatures gold volatilises as a reddish vapour. According to Elsner, pure gold painted on pieces of porcelain and fired, volatilised completely at the temperature of the porcelain kiln (2,500° to 3,000° C). The volatility of gold is increased by the presence of foreign metals. According to Napier the loss of gold with 12 per cent. of copper when heated to its melting point amounted to 0·234 per cent., with 10 per cent. of copper at a higher temperature 0·21 per cent., and at the highest possible temperature 0·8 per cent.

Gold has the property of absorbing gases, in the solid form when heated to redness, in the spongy form at ordinary temperatures. According to Graham gold cornets heated to redness absorbed 0·48 per cent. by volume of hydrogen, 0·29 per cent. of carbon monoxide,

0·16 per cent. of carbon dioxide, and 0·19 to 0·24 per cent. of gas, chiefly nitrogen, from the air. Spongy gold precipitated by oxalic acid, evolved when heated to redness, 0·704 per cent. by volume of gas, consisting of carbon dioxide, carbon monoxide and a little oxygen.

The thermal conductivity of gold, silver being 100, is given as between 60 and 103 (according to Depretz 103, Calvert and Johnson 98, Wiedemann and Franz 60).

The specific heat is between 0·0298 (Dulong and Pettit) and 0·03244 (Regnault).

Its electrical conductivity is 73 at 21·8° C. according to atthiesen, silver at 0° C. being taken as 100.

With respect to the effect of foreign substances on gold, it is to be particularly noted that lead, bismuth, cadmium, antimony, aresenic and tin render gold brittle when present even in minute quantities; $\frac{1}{2000}$ of lead, bismuth or tin already produces brittleness in gold. According to Hatchett gold with 0·00032 per cent. of antimony is no longer malleable. Tellurium causes brittleness in gold. Zinc also renders gold brittle, but if the gold contains at the same time silver and copper, an admixture of 5 to 7 per cent. of zinc does not affect its malleability. Platinum only diminishes the ductility of gold when it is alloyed with it in large quantities (over $\frac{1}{2}$). Osmium and iridium, on account of their high melting points, will not alloy with gold, but remain as grains in the molten mass, and affect the working of the gold on account of their great hardness.

The Chemical Properties of Gold and its Compounds, that are of Importance in its Extraction

Gold oxidises neither at ordinary temperatures, nor at a red heat. It forms two oxides (Aurous, Au_2O, and Auric, Au_2O_3), neither of which are well known.

It is soluble neither in sulphuric, nitric nor hydrochloric acid, but dissolves in solutions containing chlorine or bromine, in solutions of sodic, calcic and cupro-sodic hyposulphites, in solutions of cyanides, especially of cyanide of potassium, and in small quantities at 100° C. in ferric and cupric salts in the presence of alkaline carbonates and excess of carbon dioxide.

Dry chlorine gas does not attack molten gold, but attacks leaf gold at 300° C. and pulverulent gold at ordinary temperatures.

Gold dissolves freely, however, in solutions containing chlorine, like chlorine water, or that generate chlorine, like, *e.g.*, aqua regia, mixtures of hydrochloric acid with chromic acid, antimonic acid,

peroxides or nitrates, or mixtures of nitric acid with salammoniac or salt.

Auric chloride, $AuCl_3$, is thereby formed. This salt, which forms on evaporation a dark ruby-red or reddish-brown mass, is decomposed on heating to 180° C. into aurous chloride, AuCl, and chlorine. When heated to over 200° C, aurous chloride is decomposed into chlorine and gold.

Bromine acts like chlorine, only more slowly.

Aqueous solutions of iodine do not attack gold, but an etherial solution attacks it even in the sunlight; the effect is much greater when the temperature is raised and the pressure increased.

Hyposulphites of potassium, sodium, calcium and magnesium dissolve metallic gold with the formation of double salts; sodic hyposulphite, for instance, produces the salt $3Na_2S_2O_3$, $Au_2S_2O_3+4H_2O$. According to Russel, 1000 cc. of sodic hyposulphite solution of the most varying degrees of concentration will dissolve 0·002 gram of gold (or 1 gallon of solution dissolves 0·14 grain). The dissolving power of the hyposulphites of calcium and magnesium is similar, but of potassium is less; that of the double salt of sodium and copper is the same as of the hyposulphite of sodium (Russel).

Cyanide of potassium and sodium dissolve gold as a double salt, potassium cyanide, for instance, as auro-potassic cyanide ($KAuCy_2$).

Gold is but feebly combined in its solutions, and is accordingly precipitated by a whole series of substances, such as phosphorus, sulphur dioxide, nitrogen, nitrous acid and nitrites, arsenious acid, antimonious chloride, mercury, silver, palladium, platinum, the common metals, carbon, ferrous salts, stannous chloride, and many organic compounds, such as oxalic acid. Sulphides, such as pyrites, galena, sulphide of copper, zinc blende, cinnabar, stibnite and sodic sulphide precipitate metallic gold from a solution of the chloride. From solutions of auro-potassic and auro-sodic cyanide gold is thrown down as metal by the metals of the alkalies, by aluminium and by zinc.

In gold extraction, ferrous salts (sulphate and chloride), charcoal, sulphuretted hydrogen and sulphides are used to precipitate gold from its solutions, zinc being used in the case of dilute auro-cyanide solutions.

Gold does not combine with free sulphur. Sulphuretted hydrogen throws down from gold solutions a brownish-black precipitate consisting of sulphide of gold, of metallic gold and of sulphur; in the cold it consists mainly of sulphide of gold, but decomposes on heating, all the gold separating in the metallic state. Sulphide of gold dissolves

in alkaline sulphides forming a sulpho-salt; this is also formed when gold is fused with alkaline carbonates and sulphur.

Gold forms alloys with most metals.

Gold readily alloys with mercury in all proportions, forming so-called *gold-amalgam*, which is soluble in mercury. Mercury not only takes up gold very readily but is also capable of separating it mechanically from substances lighter than the former. If, for instance, sand containing gold is thrown on to a bath of mercury, the particles of gold will sink in the mercury, whilst the sand floats on its surface. The solubility of gold amalgam in mercury increases with the temperature. At ordinary temperatures 1,000 parts by weight of mercury will dissolve about 0·94 parts of gold.[1] The gold-bearing mercury can be decomposed by heating, into gold and mercury, the mercury volatilising at about 360° C., whilst the gold remains behind as metal; the mercury can be recovered by the condensation of its vapour. Mercury thus distilled off from gold amalgams carries a little gold with it, under ordinary conditions about 0·005 parts by weight of gold to 1,000 of mercury (H. Louis, *op. cit.*).

As mercury is fluid at ordinary temperatures, and does not combine with the majority of the constituents of gold ores, and as it can moreover be separated again from gold at a comparatively low temperature, it forms the most universally employed means of extracting gold from its ores.

With silver gold alloys in all proportions. Native gold is very generally alloyed with more or less silver.

Whenever, therefore, silver is contained in ores or furnace products, it always takes up any gold that may be present when treated by any method of fusion. In gold extraction, auriferous silver or argentiferous gold is therefore often produced. The alloy of gold and silver thus obtained is subsequently *parted*, as will be described further on (p. 842).

Gold and silver may be separated, as has been stated under the head of Silver (p. 465), by converting the silver into nitrate, sulphate, chloride or sulphide, as also by means of electrolysis.

Lead and gold fuse together readily in all proportions; molten lead also extracts gold from its combinations with great readiness. On account of the oxidisability of lead at high temperatures to a fusible oxide, gold and lead can be separated in the same way as silver and lead, by cupellation.

As most lead is silver-bearing, gold that is extracted by means of

[1] H. Louis, *A Handbook of Gold Milling*, 1894, p. 81.

lead is generally alloyed with silver. As compared with mercury, lead has the disadvantage that it cannot be used for gold extraction at ordinary temperatures, but must first be melted and kept in the molten condition by the application of a considerable quantity of heat before it can act on the gold. It forms, nevertheless, an excellent medium for collecting gold and silver in smelting ores and artificial products containing gold and silver. It is less often used in the metallic state than in the state of ores and metallurgical products, which are reduced by the smelting operations.

Copper alloys readily with gold; the latter metal can be extracted from these alloys by means of lead. Gold can also be separated from copper by dissolving the latter in acids or by means of electrolysis. Copper is used for collecting gold in the treatment of copper ores or cupriferous furnace products containing gold and silver, more rarely in the treatment of ores that do not contain copper; it is used in the form of copper ores or copper mattes.

Zinc also combines readily with old; the zinc may be removed from the alloy by distillation, by solution, by oxidation, and by electrolysis. It is not used for the direct separation of gold from ores, but an alloy containing gold, silver, lead and zinc is obtained when auriferous work-lead is desilverised by zinc. Here gold passes with copper into the first alloy that separates out, which is worked up for auriferous silver.

Gold Ores

Gold occurs in nature both in the native state and combined with tellurium.

The real ore of gold is native gold.

Native Gold

This is generally alloyed with silver which may amount to 39 per cent.; it also often contains smaller quantities of the platinoid metals, iron, copper, lead, bismuth and mercury.

Native gold occurs in part *in situ* in its original deposits, in part in beds of sand and gravel which have been formed by the destruction of the former. Gold of the first class is called *reef-gold*, of the second *alluvial gold*.

Reef-gold is generally found disseminated in quartz, accompanied by brown hæmatite in the upper portions (gossans) of the deposits, and by sulphurets in the lower portions, especially iron pyrites, also arsenical pyrites, zinc-blende and galena. It also occurs in very

small quantities in many deposits that carry pyrites or blende, *e.g.*, Rammelsberg, Lautenthal, Freiberg and Reichenstein.

Alluvial gold occurs as dust, grains, scales, and larger pieces (*nuggets*) in alluvial deposits, which form beds of sand, gravel or breccia either upon the surface (shallow placers) or at greater or less depths beneath it (deep placers), and which have been produced by the destruction of gold-bearing deposits. It also occurs in the sands of many streams and rivers, having been washed out of the rocks on their banks. Amongst the foreign substances with which alluvial gold is mixed may be named quartz, clay, mica, chlorite, serpentine, ilmenite, magnetite, chromite, garnet, spinel, zircon and platinum. Important alluvial deposits occur, for example, on the western flanks of the Sierra Nevada in California, where they are 650 feet in thickness and fill the valleys of Pliocene rivers.

In the gravels of California, nuggets, according to Eggleston, of 2,250 ounces troy, of Australia (Ballarat in Victoria) of 2,958 ounces, and of the West Indies of 43,400 ounces have been found.

The most important localities for native gold are: Australia, especially the colonies of Victoria (Ballarat, Bendigo), Queensland (Mount Morgan, for a time the richest gold mine in the world, Gympie gold fields), West Australia (especially Coolgardie), New South Wales and New Zealand, in all of which countries it occurs both as reef- and as alluvial gold; North America, especially the United States, British Columbia, and Nova Scotia. Of the United States the principal producers are: California, especially on the flanks of the Sierra Nevada (reef and alluvial), Colorado, Nevada (Washoe, Carson river), Oregon, Idaho, Montana, Utah, Dakota, Arizona, Wyoming, &c. In South America gold is found in Brazil, the Guianas, Chili, and Peru; in Africa, chiefly in the Transvaal, in South-West Africa, and the Gold Coast; in Asia, in India, Turkestan, East and West Siberia. In West Siberia it occurs both in reef and alluvial deposits at Beresov, Miask, Troitsk, Goroblagodat, Tagil, Bisersk, Kishtimsk, as also in the districts of the Bashkires, Teptjares, and Cossacks; in East Siberia in the districts of the rivers Yenisei, Amur, Olekma, Witim and Kara.

In Europe gold occurs only in relatively small quantity. It occurs in Russia (the Urals), in Siebenbürgen (Abrudbanya, Vörös-patak, Butzum, Vulkoy, Ruda, Brad), also in Carinthia (Heiligenblut), Salzburg (Rauris and Gastein), Italy (Pestarena), Finland and Norway. In England it occurs in Wales. In Germany only in very unimportant quantities in the sands of some rivers (Rhine, Eder), as also in some deposits of pyrites.

Compounds of Gold with Tellurium

These but rarely occur in any quantity; among them are Graphic Tellurium or Sylvanite $(AuAg)Te_2$, Foliated Tellurium or Nagyagite $(Pb, Au)_2 (S\ Te\ Sb)_3$, and White Tellurium $(Au\ Ag\ Pb)\ (Te\ Sb)_3$. These ores occur at Nagyag and Offenbanya in Siebenbürgen, in the Altai, in California, in Boulder County, Colorado, in West Australia, and other places.

Auriferous Metallurgical Products.

The chief metallurgical products that furnish material for the extraction of gold are mattes, black copper, dross, slags, and alloys of silver and gold. Gold is but rarely extracted from pyrites residues.

The Extraction of Gold

Gold may be extracted from its ores, either direct by washing, or by metallurgical processes; in the latter it is combined with mercury, lead, silver or copper, or brought into aqueous solution. The extraction may be performed n the dry way, in the wet way, or by means of electrolysis.

We have therefore to distinguish:

1. Extraction of gold by simple washing.
2. Extraction of gold in the dry way.
3. Extraction of gold in the wet way.
4. Extraction of gold by means of electrolysis.

The extraction by simple washing is effected by dressing gold-bearing sands, gravels, or ores.

The extraction of gold in the dry way is effected by converting the gold into a gold-lead or gold-lead-silver alloy and cupelling it.

The extraction of gold by combined wet and dry methods may be effected by:

(*a*) Obtaining the gold as a gold-mercury alloy.

(*b*) Obtaining the gold in aqueous solutions.

(*c*) Obtaining the gold as a gold-silver or a gold-silver-copper alloy, and dissolving the silver and copper out of these alloys.

The extraction of gold by electrolytic methods is effected by obtaining the gold as a gold-silver or gold-copper alloy, and separating these metals from the gold by means of electrolysis.

The separation of gold and silver is known as *parting*, and will be described independently of the other methods of gold extraction, after these latter have been dealt with.

The selection of a method of gold extraction depends on the mode

of occurrence of the gold and the nature of the substances intermingled with it.

Extraction of the gold by washing alone is only possible in the case of ores carrying native gold. Except for the separation of the gold that occurs in coarse grains or larger nuggets in alluvial deposits, by handpicking or washing, this method is now only used exceptionally and in uncivilised countries, because of the heavy losses entailed by it. Washing is, however, often combined with amalgamation of gold ores.

The dry method of gold extraction consists in smelting gold ores or auriferous furnace products with lead, lead ores or lead-bearing furnace products.

This method should be employed not on pure gold ores but on auriferous and argentiferous lead ores; it can also be used with advantage for auriferous and argentiferous copper ores.

It would only be used on pure gold ores, where lead ore and fuel are cheap, or where the other methods are not applicable owing to the character of the gold ore itself.

Extraction of gold by means of mercury, so-called amalgamation, should be employed whenever the main proportion of the gold present is capable of being absorbed by mercury. This is the most general, simplest and cheapest method of gold extraction, but often fails with ores which contain the gold in a fine state of division or enclosed in pyrites.

Extraction of gold by means of aqueous solutions (as chloride or as auropotassic cyanide) is employed when the gold is not completely extracted by amalgamation, as is often the case with pyritic ores. This method may often be used with advantage where amalgamation fails and smelting processes are too expensive; it is frequently combined with the last described method.

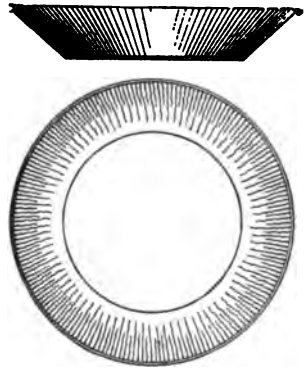
The extraction of gold in the form of gold-silver or gold-copper alloys, out of which the silver and copper are subsequently dissolved, is a combination of smelting methods or wet methods with parting. Auriferous copper is obtained by smelting gold-bearing copper ores, or gold ores with copper ores or mattes. Auriferous silver is obtained by treating gold-bearing silver ores with lead; argentiferous gold is obtained in most methods of gold extraction. The silver and copper are dissolved by acids leaving the gold behind.

The extraction of gold by electro-metallurgical methods has so far only been practised with advantage for the treatment of gold alloys, especially of gold-copper and gold-silver alloys, and is also a form of parting.

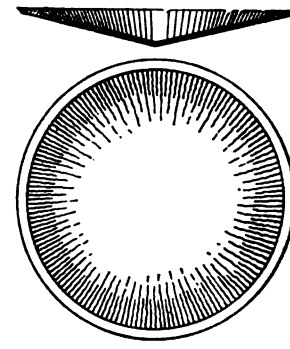
I. Extraction of Gold by Washing.

The extraction of gold by washing or dressing alone is only quite exceptionally used in civilised countries on account of the heavy losses of gold entailed by it, which may amount to 50 per cent. In combination with amalgamation it is, however, the method most commonly used.

In California gold prospectors use a pan (Figs. 521 and 522) to test gold-bearing rock and to extract the finest gold on a small scale. It is made of black sheet iron, usually Russian sheet iron; in Australia the pan is generally made of sheet tin. In Mexico and South America a wooden dish in the shape of a flattened cone 16 inches in diameter and 2 inches deep, known as the *batea*, (Figs. 523 and 524), is used. Similarly shaped wooden dishes are used by uncivilised or semi-civilised tribes in most parts of the world, *e.g.*, Borneo, Malay



Figs. 521 and 522



Figs. 523 and 524.

Peninsula, West Africa, &c.; these are sometimes segments of spheres instead of being conical.

In California and Australia the cradle or rocker and the long tom were largely used at one time. The cradle is a box provided with a sieve in the upper part, the whole resting on rockers, so that it can be rocked by means of a handle. The gold-bearing gravel is thrown into the sieve and water is thrown on; the pebbles are retained in the sieve, or carried away from it by the water, whilst the finer parts are carried through it by the water, which washes away the lighter portions over the inclined bottom, whilst the heavier containing the gold are retained by transverse slats, known as *riffles*. The construction of a cradle is shown in Figs. 525 and 526, in which *s* is the sieve, *t* the bottom of the cradle, divided by the riffles (*v*) into a

number of separate compartments; *y* are the two rockers, resting on the floor pieces *z*. *H* is the handle by which the apparatus is rocked.

The coarser pebbles escape by the shoot *G*, the finer lighter portions by *K*. With fine gold the loss of gold is very great. A man can wash 1½ cubic yards of gold-bearing sand per day in the cradle.

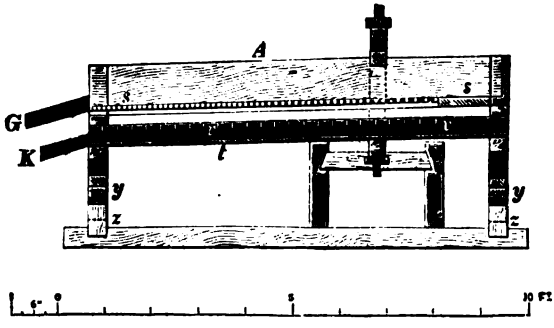


FIG. 525.

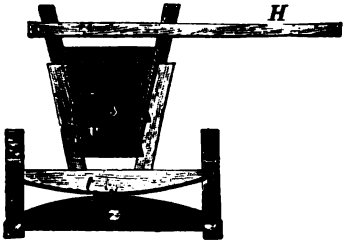


FIG. 526.

Very often this machine is used as a crude amalgamating contrivance by pouring a little mercury into the riffles. In California its use is now practically confined to Chinamen, who are rewashing old tailing heaps that have already been washed one or more times.

The long tom, too, is now almost confined to the Chinese. It consists of two troughs, of which the lower lying one is furnished with cross-riffles on its inclined bottom. The upper trough is 14 feet long and has a slope of 1 inch to the foot; the upper end is 20 inches, the bottom end 30 inches wide; its lower end is closed by a sieve that retains the coarser pieces, pebbles, &c. The lower trough is 12 feet long and 3 feet wide, and has the same slope as the upper one. By means of a strong stream of water the material thrown in at the upper end of the upper box, is carried through both boxes, the gold being caught in the riffles of the lower box. Two men with the long tom can do five times as much work as with the cradle.

The puddling tub or puddling box has been chiefly used in Australia, where the alluvial contained much tenacious clay and where water was scarce. It consists of a tub or a box, according to the size of the machine, in which rakes are made to revolve by hand, animal or machine power, according to size, as in an ordinary clay pug mill. The alluvial is stirred in this with water till the clay is suspended in the water, when the contents are run through a trough fitted with riffles. The water is generally run into a settling pit and used over again.

At present the *sluice* is the appliance most used in the United States. It consists of a series of troughs or boxes 1 foot 4 inches to 1 foot 9 inches wide and at least 9 inches deep. Each box is 12 feet long, and they are connected so as to form long troughs, sometimes several hundreds of yards in length, the inclination being from 8 to 20 inches to the 12 foot box. They are furnished with either longitudinal or transverse wooden slats or riffles, which are wedged into their places, and which help to disintegrate the clayey matter. At intervals so-called *undercurrents* are inserted, to separate the coarser pebbles, &c. These are formed by replacing the bottom of a box by a grating, known as a *grizzly*, and leaving the end of the box open. Underneath the grating there is a trough at right angles to the main sluice, which opens into another trough or box parallel to the main direction, and which forms the continuation of the sluice. The finer portions fall through the grating into the cross sluice, which is very wide and gives an opportunity for the settling of any fine gold, whilst the sand, &c., is carried through the undercurrent into the boxes that form the continuation of the main sluice; the larger pebbles that cannot pass through the grizzly, pass over it and out through the open end of the upper main box on to a dump.

The gold is caught by the cross riffles. Mercury is also generally sprinkled into these so as to combine amalgamation with washing. The ore to be washed is shovelled in at the head of the sluice and is carried along by the current of water. The sluice is considered to be the best contrivance for washing gold-bearing gravels.

In Russia, washing appliances, consisting generally of pug mills or drums, followed by trommels and strakes, are used, and are driven by steam or water power.

Where water is very scarce, *e.g.*, in Western Australia, alluvial gold is sometimes dressed by pneumatic instead of hydraulic methods, by winnowing and dry-blowing the gravels. Machines have been used, of which Wetzlar's Tierra Seca machine is typical; in it the ore is led on to an inclined shaking sieve, upon which lies a layer of

shot, through which a powerful fan sends an upward stream of air; the gold passes through the bed of shot and the screen, whilst the lighter sands kept up by the air, pass over the bed. This machine has been used in Western Australia, but no data as to its performance are available.

The gold obtained by dressing often retains magnetite, ilmenite and chromite, together with other specifically heavy minerals. It is freed from these substances by fusion with potash, borax and nitre. The magnetite is sometimes removed by the magnet before melting, which is usually performed in graphite crucibles. Impure gold may also be treated in the lead bath of a cupelling furnace.

II.—Extraction of Gold in the Dry Way

This process consists in alloying the gold with lead and cupelling; as the lead always contains silver, the result is a silver-gold alloy that has to be parted.

The alloying of gold with lead (called in German *Verbleiung*, *i.e.*, "leading") is performed as in the case of silver. It may be effected either by introducing ores into a bath of lead, or by smelting the ores with lead-bearing fluxes, or by first smelting the ores for matte and then smelting the latter with fluxes containing lead.

The introduction of pure gold ores into a lead bath is only exceptionally practised, but this may be done in the case of ores containing considerable quantities of gold and silver, the operation being performed as in the case of silver ores.

Smelting the ores with lead-bearing fluxes for work-lead is performed as in the analogous process with silver ores already described (page 470). Ores poor in gold and silver are first smelted for matte, which is treated as in the case of silver.

If the gold ores contain copper, a part of the gold alloys with the copper, either in the form of copper matte or of black copper.

By means of zinc, auriferous lead can be enriched just as argentiferous lead can be. When argentiferous lead, that also contains some gold, is being enriched in silver, the gold accumulates in the zinc that is first added. After the zinc has been removed from the alloy, an auriferous lead is left, which is cupelled in order to extract the gold from it.

The cupellation of auriferous or auriferous and argentiferous lead is identical with that of argentiferous lead.

The treatment with lead of gold and silver ores, or of auriferous silver ores, is practised at Schemnitz, Nagybanya, and Zalathna in

Hungary, Freiberg in Saxony, and Andreasberg in the Upper Harz. These processes have already been described (page 474).

At Zalathna (page 482) a work-lead is ultimately produced from auriferous pyrites that has the following composition :—

Pb	99·346
Sb	0·018
Cu	trace
Ag	0·326
Au	0·310
Fe	trace

It is cupelled in German cupellation furnaces fired with wood. The first charge of work-lead is 2·4 to 2·6 tons, and it is raised by subsequent charges to 8 to 9 tons. The loss of lead is 8 per cent. The *blicksilver* produced contains 97·5 per cent. fine silver and gold, the alloy containing 50·4 per cent. of fine gold.

III.—Extraction of Gold by Combined Wet and Dry Methods

A. Extraction of Gold in the Form of a Gold-Mercury Alloy

This process is known as *amalgamation*. It consists in combining the gold with mercury, and in decomposing the gold-mercury alloy or amalgam thus obtained, by heating it, whereby the gold is obtained as metal, whilst the mercury is volatilised as vapour, and again condensed. The mercury does not only alloy with the gold, but also separates it mechanically from the substances with which it is intermixed; when crushed gold ores are treated with mercury, the particles of gold sink in the latter by reason of their high specific gravity, whilst the gangue floats on the surface.

Amalgamation is applicable to ores that contain gold in the native state and free; ores that carry gold enveloped in pyrites have to be calcined before amalgamation. Chloride of gold, contained in ores after a chloridising roast, is decomposed by mercury with the formation of mercurous chloride; the gold thus separated is absorbed by the mercury. The same substances that interfere with the amalgamation of silver ores are also injurious to gold ores. These are more especially ores of lead, bismuth, zinc and antimony, which render the amalgam pasty, and the hydrated silicates of magnesia and alumina, which tend to *flour* or *sicken* the mercury.

During the crushing that precedes the amalgamation of gold ores,

the larger particles of gold are readily stamped or rolled into thin leaves, which unite with mercury with greater difficulty than the fine dust, and are hence apt to be carried away by the stream of water (*float gold*).

When the mercury is made to attack very fine particles of ore, a certain amount of the former is readily broken up into minute spherules, which are surrounded by a film of dust, and then only reunite with difficulty into larger drops, so that they are mostly carried off in the stream of pulp; mercury in this state is said to be *floured* or *sickened*. As it will have already taken up a certain quantity of precious metals, this entails a loss of gold as well as of mercury.

When pyritic gold ores are submitted to an oxidising calcination, a thin film of oxide of iron is apt to form in some cases on the gold, which has then no tendency to combine with mercury. Gold in this condition, whether naturally or induced artificially, is spoken of as *rusty* gold; besides the above cause of rustiness, a number of others are assigned by various authorities. Chloridising roasting will remove this film, the oxide of iron being converted into a volatile chloride.

A distinction may be made between the amalgamation of gold-bearing material which does not require crushing, and of material that requires it. The crushing may be simultaneous with the amalgamation, or may precede it. In either case the ore may be amalgamated without previous concentration, during concentration or after concentration.

Amalgamation, without Previous Crushing, of the Gold-Bearing Material

(*a*) without previous concentration

This form of amalgamation was and is carried on upon a very vast scale in California, where it is combined with so-called *hydraulic mining*, a development of the sluicing already described.

The gold-bearing gravels are washed down by powerful streams of water under high pressure, and carried by the currents of water into long sluices, where they are brought into contact with mercury.

The water is collected in huge reservoirs, ponds, lakes, dams, &c.; it is then brought by means of ditches, flumes or pipes to the point where it is to be utilised; such ditch-lines are at times over 100 miles in length. These convey the water to head boxes, whence iron pipes, made of sheet-iron, about 30 inches in diameter, convey it down to distributing boxes, from which separate sheet-iron pipes distribute it to the various parts of the mine. These pipes terminate

in cast-iron nozzles, known as *monitors* or *giants*, movable horizontally and vertically by means of ball and socket joints, so that the stream may be turned in any desired direction, the movement being produced by the force of the water itself by means of a short piece of pipe projecting over the nozzle, known as the *deflector*. The stream of water is from 4 to 11 inches in diameter, under a head of 250 to 500 feet, and is directed against the banks of gravel from a

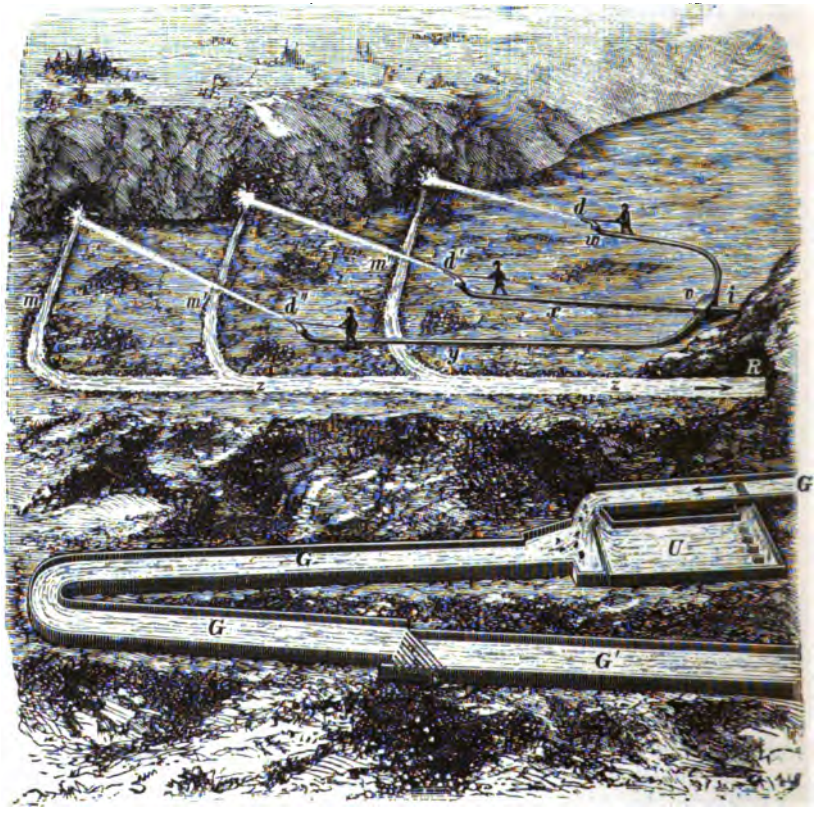


FIG. 527.

distance of 160 to 200 feet, more or less, according chiefly to the height of the bank. An idea of hydraulic mining (full descriptions and details of which will be found in T. Egleston's *The Metallurgy of Silver, Gold, and Mercury*, 1890, vol. ii., and in A. J. Bowie's *Practical Hydraulic Mining*, 1885) may be gathered from Fig. 527.

The water flows through the pipe *i* into the distributing box *v*, from the latter by the three branches *w*, *x* and *y* to the monitors *d*, *d'* and

d'', each worked by one man, by which it is projected against the face of the gravel; the construction of these monitors will be found fully described in the above cited works. The gravel loosened by the water is carried by the stream of water through the ditches m, m and m'' into the main ditch or ground sluice z, which leads them through the tunnel R into the sluice G, in which, and in the undercurrent U connected with it, the gold is amalgamated.

The sluices are made of planks 12 feet long and $1\frac{1}{2}$ inches thick, the total length depending on the nature of the gravels, and having in every case to be determined experimentally; it may vary from 100 yards to $6\frac{1}{2}$ miles (Spring Valley, California). The length of most sluices lies between 400 and 1,600 yards, the width between 3 feet and 6 feet, and the depth between 28 and 30 inches. The grade of the sluice is from 6 to 12 inches to the 12 foot box. For ordinary gravel the grade is usually 4 per cent, for very clayey or very coarse

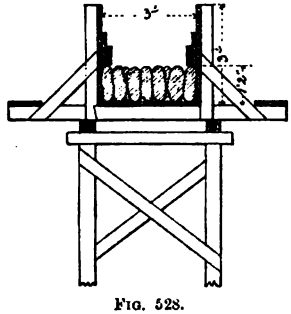


FIG. 528.

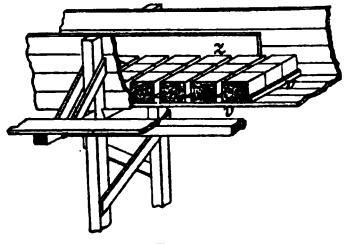


FIG. 529.

gravel, 6 per cent. to 8 per cent. In order to protect the sluice against the rough boulders of the gravel, it receives a bottom lining and a side lining. The bottom lining is either stone or block pavement, iron being but rarely used; the sides are lined with plank. The arrangement of a stone-paved sluice is shown in Fig. 528;[1] the stones are 9 inches to 12 inches thick, and consist of rock found in the neighbourhood of the mine, generally basalt. The spaces between them are filled to a certain height with gravel. Into the hollows remaining, mercury is poured to collect the gold. The side lining, which is also shown in the figure, consists of a lower board 2 inches thick, projecting 10 inches to 15 inches above the pavement, and a second board spiked over the first, 6 to 8 inches deep.

Stone pavement is far more durable than block pavement, but requires more water and a steeper grade than the latter.

A sluice paved with wood blocks is shown in Fig. 529; the blocks

[1] Egleston, *op. cit.* p. 215.

are 6 to 12 inches deep and 12 to 18 inches square; they are set in a row perpendicularly across the length of the sluice, from side to side, each row being separated from the next by a slat nailed to the bottom of the sluice; these slats, which are $1\frac{1}{2}$ inches thick and half the height of the blocks, leave grooves between each row of blocks into which quicksilver is poured to collect the gold; z is the side lining of the sluice.

Wood pavement has the disadvantage that it is rapidly worn out by the boulders rolling over it, and only lasts a short time; in full work, its life rarely exceeds 3 months. Moreover, it does not give as much free space for the mercury as the stone pavement.

In order to allow the finer particles of gold an opportunity of settling, large flat wooden boxes, the so-called *undercurrents*, are provided at intervals. These are square or rectangular, and about 15 inches deep. As their area is from 2,000 to 8,000 square feet, the water current moves very slowly in them and the fine particles of gold are thereby allowed time to settle. From these undercurrents, the stream returns to the prolongation of the main sluice.

The construction of an undercurrent is shown in Fig. 530.[1] The main sluice G, has a grating of steel bars Z which there replace the usual plank bottom; through this the finer portions drop, together with the greater part of the water, and fall into the steeply inclined trough y, which takes them into the undercurrent W. A row of wooden blocks near the head of the undercurrent serves to distribute the stream of water uniformly. The undercurrent is set on a grade of 1 foot in 12, and its bottom contains grooves or riffles of various kinds, like the main sluice, into which mercury is poured to collect the gold. At the lower end of the undercurrent the stream flows out at U and falls first into the box N, known as the *drop box*, and thence into the continuation L of the main sluice. In passing through the undercurrent the stream deposits the greater part of its gold on the bottom, where it is retained by the mercury in the riffles.

The larger stones that cannot drop through the grating Z into the undercurrent, are carried over it and through the narrower box P with a portion of the stream on to the "grizzly" Q, consisting of a grating made of rails inclined at 30°, the rails being set 6 inches apart. The grizzly lies over the drop box and projects so far that it carries all the larger boulders clear over it. The water and the smaller pebbles fall through the spaces of the grizzly, into the drop box, where they unite with the stream issuing from the undercurrent, and

[1] Egleston, *op. cit.* p. 223.

flow into the prolongation *L* of the main sluice. The larger rocks fall over the grizzly on to a dump, over a precipice or steep hill slope, at the edge of which the grizzly must always be situated. The drop box must be very strongly built, and paved with stones. The distance between successive undercurrents and grizzlies depends on the contour of the surface, and on the nature and quantity of the gravel that is being treated.

At the Sailors' Union Mine,[1] Iowa Hill Ridge, 1,615,577 parts of barren gravel have to be shifted to obtain 1 part of gold, and at

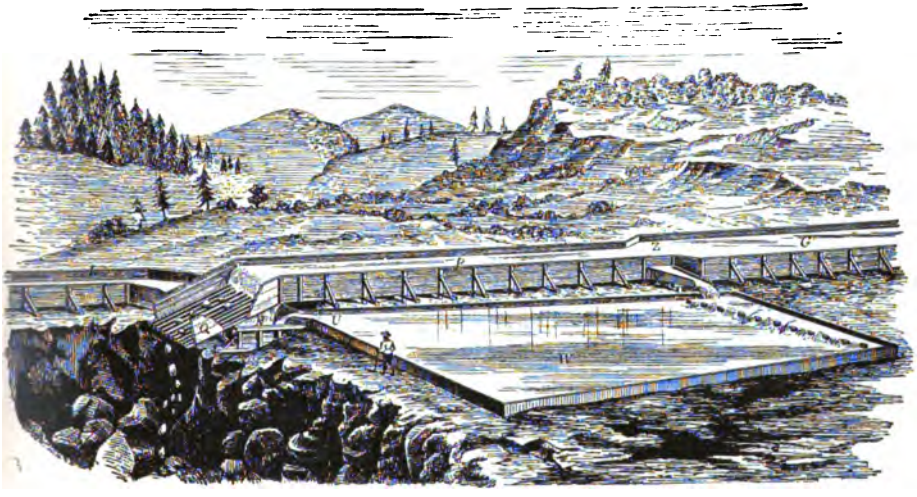


FIG. 530.

North Bloomfield Mine, 1 part of gold only was obtained from 12,107,116 parts of barren gravel.

Mercury is introduced, in the finest possible state of division, generally through a vessel with a perforated bottom, at the upper end of the main sluice, and is retained in the riffles. Generally about 1 cwt. is added daily in several lots. In a sluice about 5,000 feet long there will be at one time some 5 to 6 cwts of mercury, and some of the largest sluices may contain 2 to 3 tons. The gold amalgam is removed from the upper part of the sluice once or twice a month, and from the remainder at longer intervals of 6 weeks to 6 months. A general clean-up of the entire sluice takes place yearly. To collect the amalgam, the paving is taken up, working from above downwards; a section of the sluice is closed by means of a crosspiece,

[1] *Prod. of Gold and Silver in the U.S.*, 1882, p. 730.

mercury is poured in to collect the amalgam, and after it has taken up the latter it is scooped up by means of scoops into mercury buckets.

The greater part of the amalgam collects in the upper part of the main sluice, and an important quantity also in the undercurrents. About 80 per cent. of the total gold obtained is got from the first 70 yards of the sluice.

The amalgam is first washed with water and then stirred with mercury. The gold amalgam sinks to the bottom, whilst the base metals come to the surface of the mercury; the upper part of the bath is ladled off, and the lower part stirred with fresh mercury. The scum that rises to the surface is removed, and the residual amalgam is filtered like silver amalgam through a canvas bag to remove the excess of mercury. It is then boiled up with dilute sulphuric acid to remove any other impurities, and finally retorted.

The skimmings from the quicksilver are treated with nitric acid to remove the base metals, washed, filtered, and then treated further with the amalgam.

The loss of gold cannot be given exactly, because the richness of the gravels cannot be ascertained accurately. In the Gold River district, Placer County, the output per cubic yard [1] of gravel was taken at 4·75 cents. of a dollar; at French Corral, Nevada County, at 15 cents. in the upper gravels, and $3·50 in the lower. At Spring Valley Mine, the produce of the best portions of the gravel was between $1 and $8 per cubic yard. It is generally assumed that the loss of gold is between 15 per cent. and 50 per cent.

The loss of mercury according to Egleston [2] is between 10 per cent. and 37·5 per cent. of the total quantity employed; it is generally 10 per cent. to 15 per cent.

This method is only applicable when the gold-bearing gravels are situated sufficiently high above water-level to allow room for depositing the tailings. When sufficient fall cannot be obtained, the gravel when washed down must be elevated by means of hydraulic elevators; these work on somewhat the same principle as the injector, and force a quantity of gravel and water up an inclined pipe to a comparatively small height by means of a smaller quantity of water, delivered through a smaller pipe under a very high head. Details will be found in Egleston's work, p. 295.

The extraction of gold by hydraulic mining has caused the transfer of enormous masses of *tailings* in the form of sand and gravel

[1] The average weight of a cubic yard of gravel is 1½ to 1¾ tons.
[2] *Op. cit.* p. 271.

washed down from the banks, from the higher levels into the streams and rivers of the lowlands of California, whereby the beds of the rivers were filled up and their bottoms raised, so that the fertile low-lying flat lands were inundated, and in some instances buried under masses of these barren sands. In consequence of a series of lawsuits brought by the farming industries against the miners, hydraulic mining was finally, about 1884, prohibited by the courts in most of the important hydraulic mining districts in California, principally in those the tailings from which would ultimately find their way into the Sacramento and San Joaquin rivers. In consequence of this decision hydraulic mining almost ceased, and the returns of gold fell off considerably.[1] Relief for this leading industry of California was, however, sought, and in 1894 the so-called Caminetti Act was finally passed, which makes full provision for the resumption of hydraulic mining under the condition that miners impound all their tailings or other *débris* by means of dams or works, constructed at their own expense under the supervision of Government Commissioners; they must do this under license, which may be revoked by the Commissioners, should the retaining dams or impounding works be found inadequate to protect the rivers and lowlands. Many mines at once applied for such licenses to mine by the hydraulic method, and it is expected that hydraulic mining will once again become an important source of Californian gold production.

(*b*) AMALGAMATION WITH PREVIOUS CONCENTRATION OF THE GOLD CONTENTS

This method of amalgamation is employed for gold sands that have been enriched by concentration; it is performed in the same manner as the amalgamation of crushed and concentrated ores, to be presently described.

AMALGAMATION OF ARTIFICIALLY CRUSHED GOLD-BEARING MATERIAL

This method of amalgamation is always employed for reef-gold, and in some cases for firmly coherent, cemented masses of gold-bearing gravels, known as *cement*. It is better practised before concentration of the gold contents than after, because a considerable portion is always lost in the dressing operations. In many cases, *e.g.*, in ores that contain both free gold, and gold enveloped in pyrites, the free gold is first amalgamated, then the pyrites or sulphurets are con-

[1] *Report of the Californian State Mineralogist*, 1894, p. 13.

centrated by dressing, and either amalgamated after being calcined, or chlorinated (at times treated by cyanidation), or smelted with lead-bearing materials in the dry way. Amalgamation takes place either during the crushing of the ore and in combination therewith, or immediately after it, for getting such gold as has not already been extracted, or else after the crushing has been completed.

AMALGAMATION, PARTLY DURING, PARTLY AFTER CRUSHING

This form of amalgamation may be effected in mortars on a small scale, and on a larger scale in arrastras, mills of various kinds, and most frequently in stamp mills. By the latter method the gold is extracted rapidly, but it is apt to entail losses of gold. Naturally only such gold as is free (*free milling* gold) is extracted, and not any that may be contained in pyrites or other sulphurets.

Arrastra-Amalgamation

The arrastra, which has already been described under Silver, is used in the United States (Arizona, California, Oregon, Montana, Idaho, Colorado) in smaller establishments that work upon ores carrying only free gold or gold alloyed with silver.

The ore is first broken small in rock-breakers, stamps or Chilian mills, and then charged into the arrastra; the size of the fragments varies from dust to pieces as big as a pigeon's egg. According to the size of the arrastra the charge may be 6 to 10 cwt., together with sufficient water to form a stiff paste. After the ore has been ground for a while, mercury is added, its quantity varying with the quantity of precious metals present; it may be 1 to 1½ cwt., or for richer ores 2 to 2½ cwt. If the ores contain much silver, the amalgam is kept extremely fluid, as much as 1 lb. of mercury being charged for each ounce of silver present. Of chemicals, cyanide of potassium and wood ashes may be used to keep the mercury bright. The time of working a charge is 6 to 10 hours, according to the size of the pieces of ore charged. An arrastra 12 feet in diameter, with heavy stones making 15 revolutions per minute, and with exceptionally heavy charges (2 tons), can treat 4 tons in 24 hours.

After the amalgamation is complete the entire contents are either run into a settler, in which the amalgam is separated from the tailings as described under silver, or else the tailings are sluiced out of the arrastra whilst the amalgam is collected in it. The amalgam is filtered through canvas bags and then retorted. The tailings are either streamed over amalgamated copper plates, treated further in pans, or run to waste.

By treating ore once in the arrastra, up to 70 per cent. of the gold contents and 75 to 80 per cent. of the silver contents may be extracted.

Amalgamation in Mills

Among the mills that have been adopted to some extent in modern times in the United States and Australia for gold amalgamation, the Huntington Mill should be mentioned.

This acts both as a crusher and as an amalgamator, and is used with advantage in small operations, especially on soft clayey ores; it can

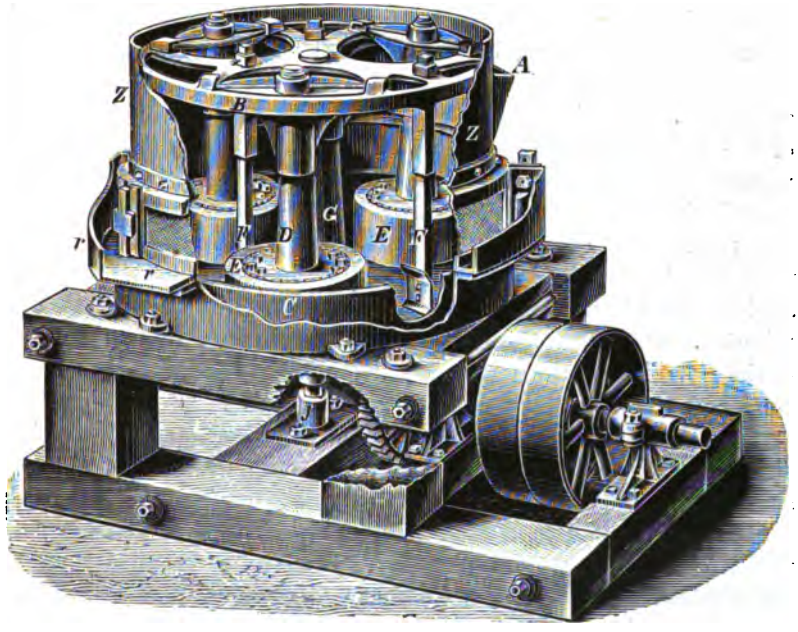


FIG. 531.

also be employed with satisfactory results for ores that carry sulphurets as well as free-milling gold. The crushed ore (*pulp*) escaping from the mill is streamed over amalgamated copper plates, upon which the free gold still retained in it, together with any amalgam that may be carried over, is caught. If the ores carry sulphurets (auriferous pyrites) these may be concentrated and caught by means of dressing machinery after they have passed the amalgamated copper plates.

The ores are broken in rock-breakers before they are fed into the Huntington Mill.

The construction of this mill is shown in Fig. 531. *Z* is a cylinder or pan of cast iron, closed above by a ring-shaped plate *B*

connected to the vertical shaft *G*, and turning with it. From the ring plate *B*, three stamps *D*, with steel shoes *E*, capable of rotating each on its spindle, are so suspended that the bottom of the shoe is 1 inch above the bottom of the pan, and that stamp and shoe are capable of swinging. When the vertical shaft *G* is rotated, stamps and shoes are carried round with it. Some distance above the bottom of the pan is a circular sieve, made in several sections, against which the pulverised ore is thrown, and through which it escapes when crushed fine enough. Outside this circular sieve is a ring-shaped gutter *r*, through which the escaping pulp flows off. The ore is fed in through the hopper *A* with the necessary quantity of water and mercury; by the rotation of the stamps the ore is thrown against the sides of the pan by centrifugal force, as well as by the action of the scrapers *F*, and here it is crushed by means of the steel shoes against the hard die-ring *C*. By the oscillating movement of the shoes, the crushed ore is pushed forward slowly and brought into intimate contact with the mercury on the bottom of the mill. The scrapers *F* prevent any accumulation of ore in the mill. The crushed ore is thrown by the movement of the shoes against the screen, through which it escapes when sufficiently comminuted. On this account it is impossible to amalgamate the whole of the gold inside the mill, and the pulp is run over amalgamated copper plates to amalgamate the rest of the gold.

The arrangement of a gold mill with amalgamated copper plates and Frue vanners for concentrating the sulphurets in the pulp, is shown in Figs. 532 and 533.

The ore broken in a rock-breaker is delivered to the automatic feeder *a* and thence to the mill *b*. The pulp escaping from the latter passes over the four amalgamated copper plates *c*, *d*, *e*, *f*, arranged one below the other, upon which the remainder of the gold is caught, and finally to the Frue vanners *g* for the concentration of the sulphurets.

Huntington Mills are in use in California, Oregon, Alaska, Idaho, Montana, Utah, Colorado, Arizona, New Mexico, Central America, South America, and also in Australia. They have recently been introduced into Kremnitz, in Hungary. They require comparatively little power for working them—4 H.P. for treating 12 tons per day, 6 H.P. for 20 tons, and 8 H.P. for 30 tons; their diameter varies between 3 ft. 6 in. and 6 ft.

At Spanish Mine, Nevada County, California,[1] gold ore consisting of decomposed slate, clay and quartz, with only 60 cents. of gold to

[1] Egleston, *op. cit.* p. 417.

the ton, are first broken in Blake rock-breakers, and then automatically fed into 4 Huntington Mills, 3 of which are 5 ft. and the fourth 4 ft. in diameter. At 60 revolutions of the main shaft per minute, the larger mills treat 35 to 40 tons per day, the smaller

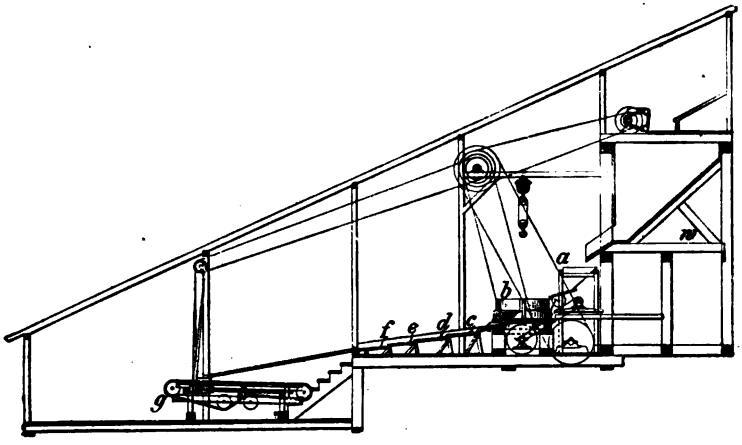


FIG. 532.

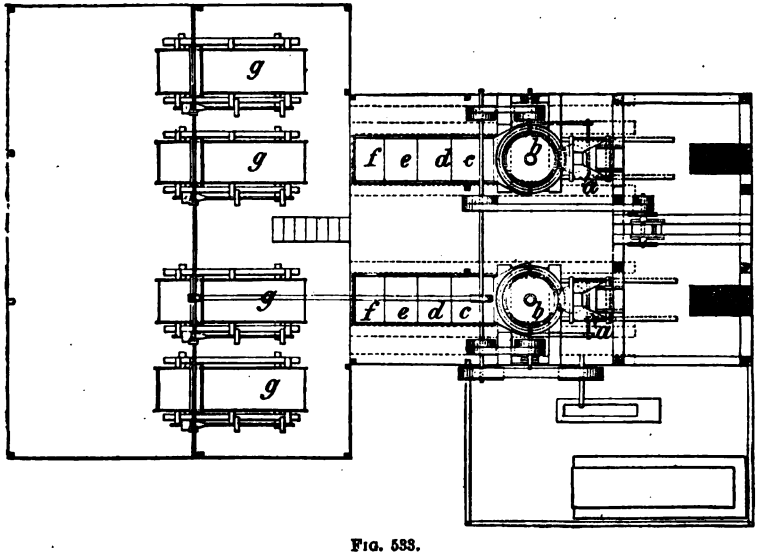


FIG. 533.

30 tons. The circular screen lasts only 4 days, the bottom and the ring-die a year. The amount of mercury charged is 1 ounce to 4 tons of ore. Of the gold, 45 per cent. is got in the mill, 55 per cent. on the amalgamated copper plates. The tailings escaping

from the latter run to waste; the loss of mercury amounts to 1 ounce to each 15 to 20 tons of ore. Crushing and amalgamating costs here, under exceptionally favourable circumstances, about 12 pence per ton of ore.

At the Kremnitz United Caroli- and Stadt-Mines, near Kremnitz, in Hungary, gold quartz with 3 per cent. of pyrites, 4 dwt. 14 grs. to 5 dwt. 5 grs. of gold, and 13 dwt. 2 grs. of silver to the ton, is being worked.

The ores are broken in Blake and Dodge rock-breakers, having a capacity of 3 to 5 tons per hour, down to pieces 2 inches cube, and are then fed into the Huntington Mill by means of a Tulloch ore feeder. This mill, at 70 revolutions per minute, absorbed 8 H.P. and treated 12 tons of ore in 24 hours, the screens having slots 0·012 inch wide. Together with the requisite water the mill holds 20 lbs. of mercury, 77 grains of mercury being also added every 10 minutes. The escaping pulp runs over 4 amalgamated copper plates on to Frue vanners, of which there are two for each mill. The head plate of these Frue vanners consists of an amalgamated copper plate; each vanner absorbs ½ H.P. On these the auriferous pyrites are collected; the escaping tailings are still further treated on buddles. The auriferous pyrites collected by these dressing operations contains 19 dwt. 14 grs. of gold and 1 oz. 19 dwt. 5 grs. of silver to the ton, and is smelted with lead at the Schemnitz Works.

The gold amalgam is cleaned out from the mill every month, whilst the copper plates are cleaned up every other day. The amalgam is retorted in bell-retorts, to be subsequently described.

The yield of gold in amalgam and concentrates is equal to 70 per cent. of that in the ore. The loss of mercury is ¼ oz. to the ton of ore. The steel ring-die in the mill lasts 3 months, the rings of the stamp heads 6 weeks.

A recent mill provided with a mercury reservoir is the Crawford Mill. Its construction is shown in Fig. 534.[1] The ore passes through the hopper $\mathfrak{A}$ on to the rotating table $\mathfrak{F}$, and thence between the iron balls $\mathfrak{E}$, that rub it to powder. The latter passes through openings $\mathfrak{N}$ into the receiver $\mathfrak{G}$, filled with mercury, in which the free gold is retained, whilst the ore freed from its gold re-enters the mill by one of the openings $\mathfrak{N}$ by the aid of a current of water from below, thence passes through the annular space $\mathfrak{B}$, overflows at its upper end, and escapes by the shoot $\mathfrak{D}$. At 100 revolutions per minute of the revolving table, the mill is said to treat 8 to 12 tons

[1] *Dürre, Zeitschr. d. Vereins deutscher Ing.* 1893, p. 902. *American Metallurgy at the World's Fair in Chicago*, 1893.

of ore in 24 hours according to the character of the ore; this also regulates its yield, which is said to be 65 to 98 per cent. of the gold contents. Results obtained in actual practice are not known to the author; this mill has not come at all into extended use.

Stamp Mill Amalgamation

Stamp mill amalgamation consists in crushing the gold-bearing ore in a stamp mill, and in feeding mercury in small quantities into

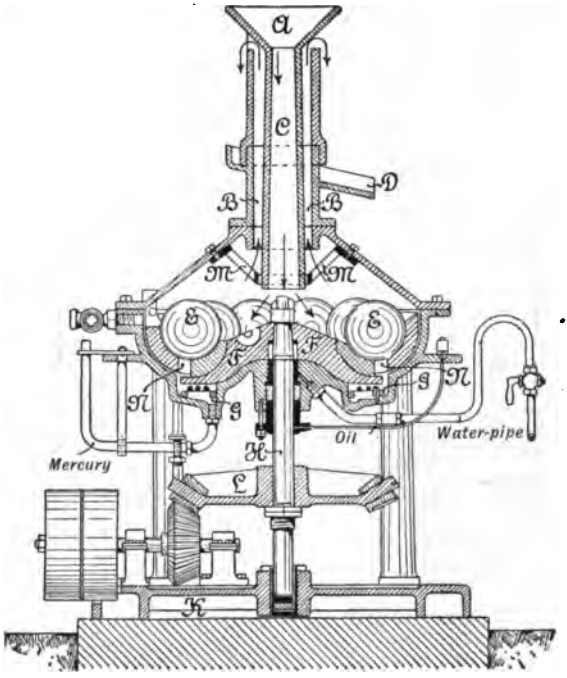


FIG. 534.

the mortar of the stamp mill whilst the crushing is going on. By regulating the water supply and by increasing the height of the level of discharge above the dies in the mortar, the mercury is kept distributed throughout the ore pulp; by the fall of the stamps it is brought into intimate contact with the particles of ore, and forms with the gold an amalgam that settles in the corners of the mortar and between the dies. The formation of amalgam is further promoted by attaching amalgamated copper plates to the inner sides of the mortar on which amalgam and free gold collect; in this case the free gold is amalgamated by the mercury on these copper plates.

As, however, all the gold is not amalgamated inside the mortar,

the pulp that issues is streamed over amalgamated plates to collect the gold not yet amalgamated, as well as the escaping mercury and amalgam. Mercury that has been rubbed on metal plates, especially on plates of copper, silver and silvered or gilt copper plates, has the property of retaining the gold that comes in contact with these plates, and of forming gold amalgam, which adheres to the plates in scaly or dendritic form.

Gold enveloped in sulphurets (*e.g.* iron or arsenical pyrites) escapes amalgamation. Accordingly when the ores contain auriferous sulphurets (*e.g.* 1 to 6 per cent. in California, and still more in Colorado),

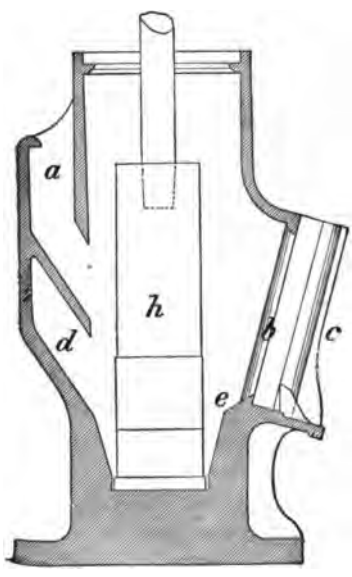


FIG. 535.

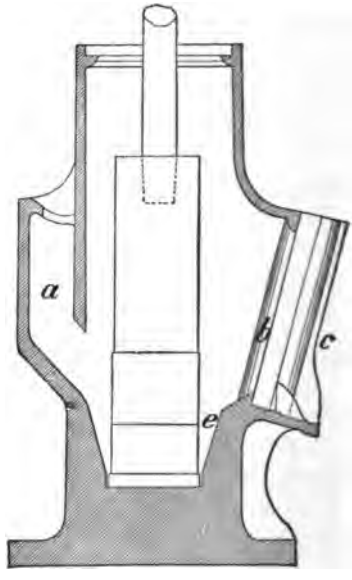


FIG. 536.

the pulp after flowing over the amalgamated tables, runs through strakes, lined with amalgamated copper plates, on to concentrating machines, generally Frue vanners, by means of which the sulphurets are obtained in the form of concentrates. These concentrates are either treated by smelting, or are submitted to cyanidation, or after calcining to chlorination, or more rarely are amalgamated after being calcined.

Stamp mill amalgamation was first practised in California and has spread thence over the whole world.

The general arrangement of these stamp mills, known as Californian stamp mills, is much the same as that of silver mills, differing but in details.[1] The construction and arrangement of rock-breakers is the

[1] See *A Handbook of Gold Milling* by H. Louis, for a description of these details.

same for gold as for silver ores. For gold ores, gyrating rock-breakers like the Gates' crusher, are now much used, and are often set in a separate building from the stamp mill proper.

Automatic feeding should always be employed, as it increases the capacity of the mill by 20 to 25 per cent., as compared with hand feeding. The Tulloch feeder (see p. 654) and the Hendy Challenge feeder are among the most popular.

The mortars are broader than those used in silver-milling, so as to be able to accommodate the amalgamated copper plates. The screen through which the pulp escapes is on one side only: the amalgamated copper plates are either at the front and back of the mortar or at the front only. They are but rarely applied to the ends. Fig. 535 shows the arrangement of a mortar with front and back plates; *a* is the feed shoot, *b* the screen, *c* a canvas curtain against which the issuing ore splashes, *h* the stamp. The amalgamated copper plates are attached at *d* and *e*; that at *d* by means of screws, whilst that at *e* is attached to a block of wood, the so-called *chock-block* that slips down underneath the screen frame, and can be lifted out.

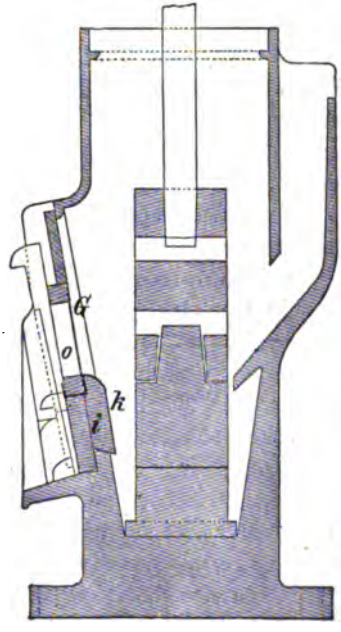


FIG. 537.

Fig. 536 shows a section of a mortar with an amalgamated plate attached to the front side only, which is fastened at *e* immediately below the screen frame. Mortars of this type are used for ores that contain base metals and require very fine crushing for the sake of subsequent concentration. In the mortar shown in Fig. 537, the chock-block is shown at *i* with the copper plate *k* screwed to it with iron screws. *G* is the screen, the screen aperture *o* being 4 feet long and 22 inches high.

The water is always admitted into the mortar box from above. The width of the mortar at the discharge level is 10 inches to 14 inches, the lower figure being taken for easily crushed ores, the higher for very hard ones. A good mortar box will last 4 to 6 years.

For screens, perforated sheet iron or woven wire screens are employed. The apertures in the sheets are either round holes or vertical, inclined or horizontal slots; they should be punched, the

burred side being inwards. These slots are generally 0·5 inch long; there are usually 8 slots to the inch. Screens with round holes are but seldom used, being almost confined to Australia; their usual diameter is 0·025 inch, with 196 holes to the square inch. Wire screens have 30 to 40 meshes to the linear inch. Screens are set in wooden screen frames and placed so as to slope outwards. The distance between the lower edge of the screen and the top of the die (known as the *depth of discharge*) should be at least 7 inches.

Screens generally last from a fortnight to three weeks.

Stamps generally weigh 650 to 900 lbs., more rarely 1,000 lbs. The height of drop varies between 4 inches and 9 inches; in California it averages 6 inches. The number of drops per minute is between 60 and 96. The crushing capacity of a stamp is between 1 and 5 tons per 24 hours. The consumption of water to a ton of ore is given as between 500 and 1,000 gallons.

Mercury is fed into the mortar box at intervals of ½ hour to 1 hour. Its quantity is so calculated that the gold-amalgam is plastic, as it adheres best to the amalgamated plates in this condition. If it is fluid it does not adhere to the plates. Each 5 stamp battery requires ¼ to ½ lb. of mercury in 24 hours.

According to the richness of the ore the amalgam is cleaned off the inside plates at intervals varying from a few days to a fortnight.

Of the whole of the gold caught as amalgam, ½ to ⅔ is saved inside the mortar box, the rest on the amalgamated copper tables. The amalgam contains but small quantities of lead and copper.

The loss of mercury is small, amounting, according to Egleston,[1] to between 0·0011 lb. and 0·0044 lb. to the ton of ore.

The escaping pulp flows on to amalgamated plates, the uppermost one being 6 to 8 inches below the lower edge of the screen, and having a width equal to that of the screen. Below the upper plate or apron, there are usually several other shorter plates arranged stepwise; the last usually terminates in a sluice, lined with copper plates, which carries the pulp to settling tanks, or to concentrating machinery, if the ore carries sulphides.

The first plate or *apron* has a grade of at least 3 inches in 12 feet and is 5 feet to 6 feet 6 inches long; the succeeding stepped plates are usually 3 feet 3 inches long and 12 inches to 18 inches wide. These plates are fastened to wooden tables. The apron which is of the full width of the screen is narrowed at its lower end to the width of the following plates or sluice. A more modern and better practice, largely followed in South Africa, is to maintain these plates for their full width from 12 to 18 feet.

[1] *Op. cit.* p. 454.

The number of plates depends on the richness of the ore and the capacity of the stamps; many mills have only one single plate, which may, however, be a very long one.

In many mills the sluices lined with amalgamated plates are also furnished with movable amalgamated plates suspended in them across the whole breadth of the sluice, at right angles to it and at short distances apart.

One of the most recent devices is Gauthier's shaking table, which consists of a table lined in the usual way with amalgamated plates, kept in a state of rapid vibration by suitable machinery. It is said that this arrangement greatly facilitates the amalgamation and retention of the gold, but no data are yet at hand to show the practical results obtained by it.

Amalgamated plates are prepared in various ways. The general method consists in coating the surface with mercury after it has been carefully cleaned. They are only thoroughly effective after they have been coated with gold amalgam; this is therefore often done from the very commencement. A second mode of preparation consists in coating them with silver amalgam: such plates are effective from the outset, because the silver amalgam is gradually replaced by gold amalgam. A third form consists of electro-silvered copper plates, which are coated with a thin film of mercury. For every square foot of surface one ounce of silver is used. Such plates work well from the beginning, and are the kind most used. The copper plate employed should be at least $\frac{1}{8}$ inch in thickness.

Before being used the plates must always be carefully cleaned; by washing with potassic cyanide greasy matter is removed, and by washing with salammoniac base metals are got rid of.

The gold amalgam is removed at least once a day from the plates by means of blunt knives known as *amalgam knives*, the last portions being scraped up with a sharp-edged piece of indiarubber, so as not to damage the smooth surface. After the amalgam has been taken off, the plates are rubbed up with a solution of cyanide of potassium, and then with a little mercury.

The arrangement of a mill without concentrators is shown in Figs. 538 and 539, which represents the 120 head Highland Mill in Dakota, built by Messrs. Fraser and Chalmers Limited, of Chicago.

The ore is dumped on to the grizzlies *r*; the larger lumps that do not pass through drop down to the rock-breakers *b*, whilst all that goes through falls into the hoppers and thence to the ore-feeders *f*, which feed it into the stamp mill. The escaping pulp flows over the

amalgamated copper tables *a*, and thence through the sluices *k*, lined with copper plates, into sluices with transverse riffles to catch the remaining particles of mercury and amalgam.

The arrangement of a stamp mill with Frue vanners for concentrating sulphurets is represented by the sixty head Montana Mill at Marysville, Montana, also constructed by Messrs. Fraser and Chalmers Limited, and shown in Figs. 540 and 541. The crushed ore flows out of the stamp mill over the amalgamated electro-silvered

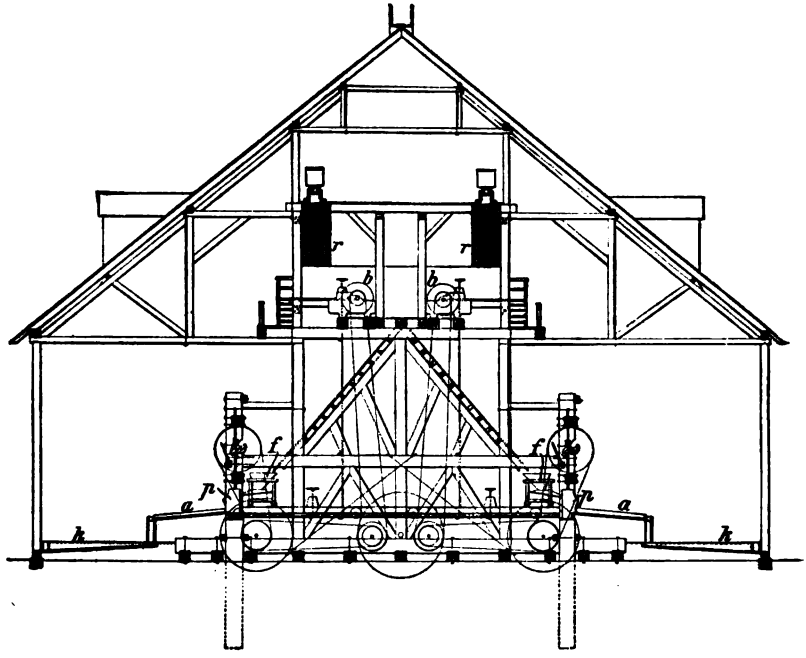


FIG. 538.

copper tables *a*, thence through the sluices *g* lined with copper plates on to the Frue vanners F and F'.

The amalgam is kneaded into balls and retorted; it is only worked up with mercury when it contains particles of iron and sulphurets.

The power required for a 10 head mill of 750 lbs. stamps making 90 drops per minute is given by Egleston (*op. cit.*) as 12 H.P., and that for its rock-breakers as 6 H.P. For a similar 20 head stamp mill the power required is 23 H.P. and for the rock-breaker 6 H.P.

The power required for any stamp mill (mill alone) may be

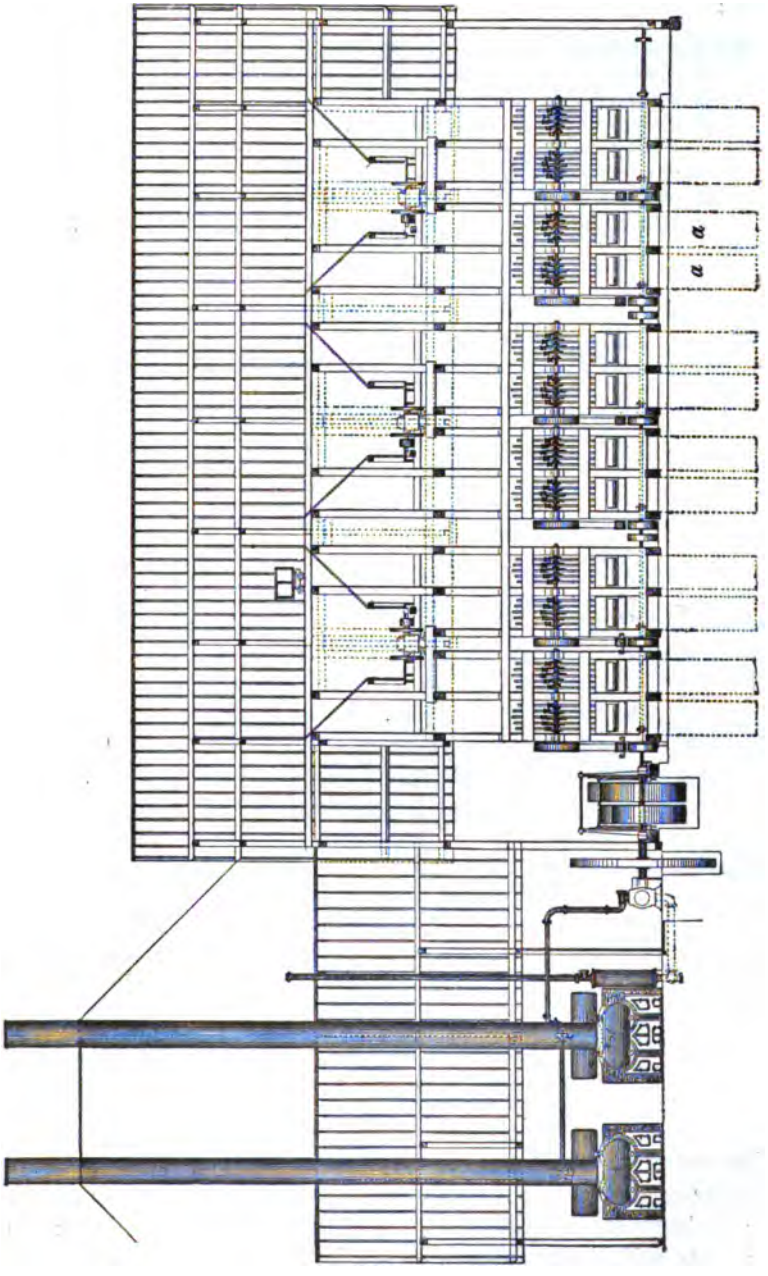


Fig. 689.

accurately calculated from the following formula of H. Louis (*op. cit.* p. 200):

Let S = number of stamps driven off one aft.
M = weight of camshaft, cams and pulley in lbs.
d = diameter of camshaft in inches.
W = total weight of one stamp in lbs.
h = height of drop in inches.
n = number of drops per minute.
k = radius of cam hub in inches.
r distance between centres of camshaft and stamp stem in inches.

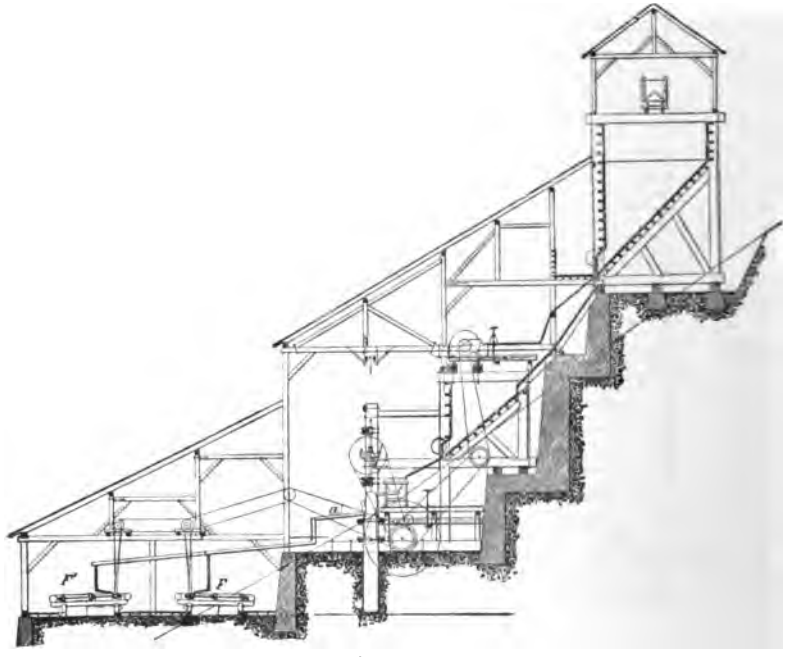


FIG. 540.

Then the total power required by this mill expressed in horse power will be :—

$$\frac{\frac{S\,n\,W\,h}{12} + \frac{S\,n\,W\,h}{3{,}600} + 0{\cdot}08\left\{S\,n\,W\left(\frac{2\,k\,h + h^2}{24\,r}\right)\right\} + \left(M + \left(\frac{h\,S}{\pi\,r}\right)W\right)\frac{d\,n}{180}}{33{,}000}$$

The water consumption is given as 72 gallons per hour per stamp.

According to Egleston, experiments have shown that the average yield of gold by stamp mill amalgamation is 70 per cent. He holds that stamp mill amalgamation is an imperfect process and that grinding deserves the preference before stamping, citing the fact

that the extraction of gold in the arrastra is greater than in the stamp mill.

At Vulkoy in Siebenbürgen, ores that contained 19 dwt. 15 grains of gold to the ton yielded 16 dwt. 8 grains or $\frac{5}{6}$.

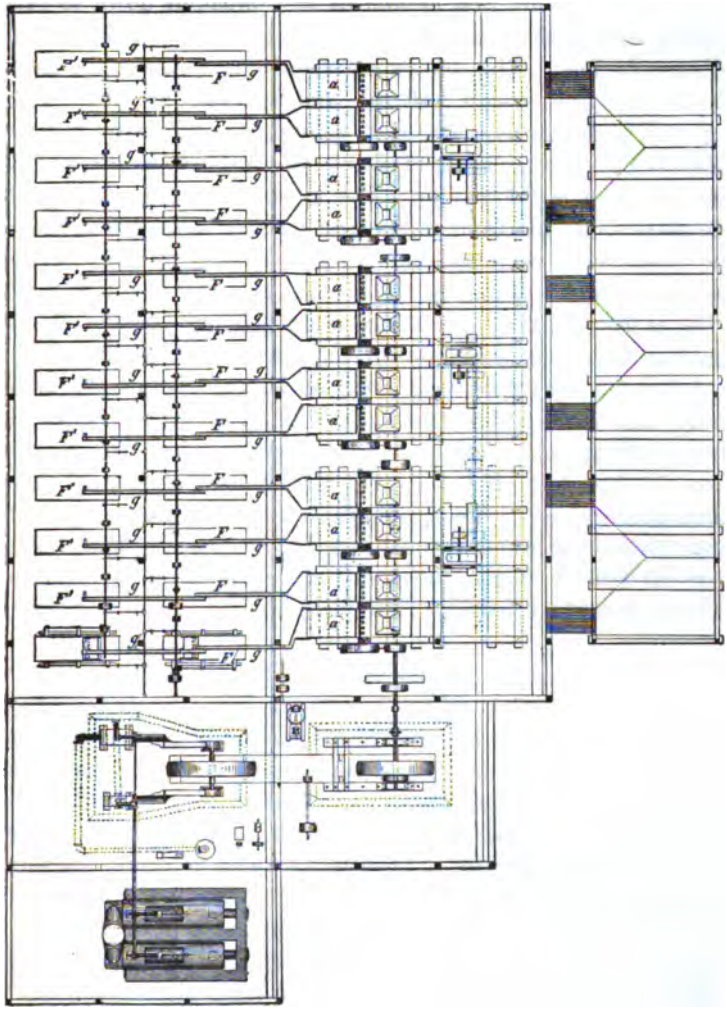


FIG. 541.

Stamp mill amalgamation is practised in California, Nevada, Colorado, Montana, Dakota, Alaska, in Australia, New Zealand, in Siebenbürgen, in the Transvaal, in India, and many other places.

A few examples may be quoted.

The Homestake mill in Dakota,[1] treats quartzose and pyritic ores, from which $4 to $5 per ton is extracted, whilst the tailings retain $0·25 with oxidised and $2·50 to $6 with pyritic ores. The Homestake has 2 mills, one with 120, the other with 80 heads of stamps. The ores are first broken by rock-breakers down to between 1½ inch and 1¾ inch cube, and then fed into the mortars by means of Challenge feeders. The stamps are 850 lbs. in weight; the shoes are made of cast iron, weigh 140 lbs., and last two months. The 80-stamp mill is driven by a 190 H.P. engine, the 120-stamp mill by one of 300 H.P. The number of drops per minute is 80 to 82, the height of drop is 8·5 inches. The mortars have an amalgamated inside plate along the front side. The screens have 8 diagonal slots to the linear inch, each slot being 0·5 inch long by 0·02 inch wide. Each stamp crushes 4 tons in 24 hours. Mercury in quantities of 3 to 6 lbs. is fed into the mortar box every 6 hours. Below the lip of the mortar box is an amalgamated copper plate in 4 pieces, 10 feet long, 4 feet 6 inches wide with a fall of 2 feet. Below this comes a mercury trap in three compartments for catching mercury. Then follows a sluice with amalgamated copper plates laid along the bottom, 14 feet long, 2 feet wide, at the end of which there is another mercury trap. Then follows a sluice 50 feet long with its mercury trap, from which the tailings run to waste. The mortar is cleaned up twice a month, the plates are cleaned up every morning, and the sluices every 4 days. The yield of gold is said to be 70 per cent.

At Providence Mine,[2] near Nevada City in California, ores with 5 per cent. to 6 per cent. of sulphurets are being treated. They are broken in rock-breakers, stamped in mortars with inside copper plates, streamed over amalgamated copper tables, and finally concentrated on Frue vanners to save the sulphurets. From the vanners the tailings run to waste. The stamps are 750 lbs. in weight; the shoes are of cast iron and weigh 136 lbs. They make 93 to 96 drops per minute, the height of drop being 6 to 8 inches. A stamp will crush 2 tons in 24 hours. The sieves have 20 meshes to the linear inch. The amalgamated copper plates are of the full width of the mortar, 4 feet long, and have a grade of 1¾ inches to the foot.

Of the gold got as amalgam, 20 per cent. is saved in the mortar, and 80 per cent. on the plates.

[1] H. O. Hofman, *Gold Milling in the Black Hills*, A. I. M. E., February, 1889. Egleston, *op. cit.* p. 459.

[2] Egleston, *op. cit.*

The sulphurets produced on the Frue vanners only contain 10 per cent. of sand. Their value for gold is $120, for silver $10. They are submitted to a chloridising roast, and then chlorinated for the extraction of the gold; the residues from this process are leached with sodic hyposulphite to extract the silver.

At the Sierra Buttes Mine, Sierra County, California, ores yielding $7·53 in free gold and containing ½ per cent. of sulphurets are crushed in 2 mills, one with 50 and one with 60 heads of stamps. The 60-head mill is driven by a Pelton wheel and has 850 lb. stamps. The shoes are of steel, weigh 176 lbs., and last 100 days, whilst the dies are of cast iron and last only 45 days. The stamps make 87 8-inch drops per minute, and crush 2⅛ tons per head per 24 hours. The screens have 20 to 30 meshes to the linear inch. The mortar has inside copper plates both back and front.

The sluice leading from the mortar and lined with copper plates is 16 feet long and 14 inches broad. The total length of amalgamated plates in the mill is 240 feet. From the plates the ore passes to Frue vanners to collect the sulphurets. Of the free gold, 80 per cent. is saved in the mortar and 20 per cent. on the plates. The sulphurets are worth $80 to $120 for gold; they are roasted and chlorinated.

The Treadwell Mill on Douglas Island, Alaska, at present the largest mill in the world, with 240 heads, is treating gold quartz carrying $5 to $6 per ton together with sulphurets. The stamps are arranged in two rows, 120 in each. The ores are broken first in Blake rock-breakers,[1] of which there are 6 to each 120 head of stamps. The stamps weigh 900 lbs., the shoes alone 154 lbs.; shoes and dies are made of chrome steel and last 250 days. The stamps make 90 eight-inch drops per minute, and crush 2½ tons per head per 24 hours. The screens have 35 meshes to the linear inch. The pulp from each mortar is discharged into a sluice 12 feet long and 2 feet wide, in which there are three amalgamated copper plates. From this sluice they enter a cross sluice with a mercury trap, and thence pass to the Frue vanners to collect the sulphurets. There are 2 vanners to every mortar. The sulphurets collected by this means contain gold to the value of $80 to $100 per ton; the gold is extracted from them by means of chlorine. The total number of men employed in the 240 head mill is 30.

The cost of treatment[2] per ton of ore in this very well-arranged

[1] During 1895 the Blake rock-breakers were replaced by Gates crushers.

[2] Directors' *Report* for Year ending May 31st, 1895, p. 9.

mill were as follows during 1895, in which year 241,278 tons of ore were crushed and 4,233 tons of concentrates were saved :—

Labour per ton of ore	$0·1689
Shoes and dies	0·0430
Mercury	0·0046
Steam power.	0·0807
Miscellaneous stores	0·0621
Cost of milling per ton of ore . .	$0·3593

The cost of treating the concentrates was $8·761 per ton of concentrates equal to $0·1547 on the ton of the original ore.

In the Transvaal, the Robinson Mill has been one of the most successful; it was till quite recently a 70 stamp mill, but 110 heads are now erected. The ore is broken at the shaft head in Gates rock-breakers and is delivered to the mill broken to about 2-inch cube. It is fed into the mortar boxes, which have inside copper plates, by means of Hendy's Challenge feeders. The battery screens have 30 meshes to the linear inch. The stamps weigh 950 lbs.; the shoes weigh 229 lbs., are made of steel and last about 3½ months, the life of the dies being nearly the same. From the battery the pulp streams over amalgamated copper plates 12 feet long and 4 feet 6 inches wide, having a quicksilver trap at the end. From the plates, the tailings pass to the Frue vanners, which collect the concentrates, and thence to settling pits, the sands thus accumulated being treated by cyanidation. The quantity of ore crushed is 4½ to 4⅝ tons[1] per head per 24 hours. The loss of mercury is about ⅛ ounce to the ton crushed.

The ore treated is the usual pyritic conglomerate of the district; it averages about 19 dwt. per ton, the total recovery of gold being about 91 per cent. The proportion of gold obtained in the various processes during the year 1894 was:

By amalgamation in the mill	76·3 per cent.
By chlorination of the sulphurets	9·8 „ „
By cyanidation of the tailings	13·9 „ „

In others of the large mills at Johannesburg, Frue vanners are not used, and the tailings are run direct from the amalgamated plates and mercury traps into settling pits, the sands from which are treated by cyanidation.

[1] The South African ton, like the American, is the short ton of 2,000 lbs.

At Vulkoy, in Siebenbürgen, Transylvania, there is a stamp mill of Californian pattern with 20 heads in 4 mortars, which is treating pyritic gold quartz with 19 dwt. 14 grs. of gold to the ton. The inside amalgamated plates are at the front side of the battery. The screens have holes 0·02 inch in width. The escaping pulp runs over amalgamated copper tables 13 feet long and 4 feet 7 inches wide, on to Frue vanners where the sulphurets are concentrated. Mercury is fed into the mortars every half hour. Amalgam is cleaned off the inside plates every fortnight, and from the outside plates every morning; of the total amount got, 75 per cent. is saved inside the mortar, and 25 per cent. outside it. The mill is worked by a 35 H.P. steam engine, of which 26 H.P. are absorbed by the stamps. Two men are sufficient to work the entire plant. During the presence of the author at Vulkoy, 35 tons of ore were treated daily with the production of 25¾ ounces of gold—or gold and silver—amalgam. The loss of mercury was with the richer ores 1 part by weight of mercury to 1 of gold won, with the poorer ores 2 parts of mercury to 1 of gold. The sulphurets were treated in the dry way at Zalathna.

AMALGAMATION AFTER PREVIOUS CRUSHING OF THE ORES

The amalgamation of ores that have been crushed, generally in stamp-mills, more rarely in arrastras, is effected in apparatus of the most diversified kinds; mortars, barrels, mills (Hungarian mills), pans, amalgamated plates and *amalgamators* of various patterns are all employed.

Amalgamation in Mortars

This is only used when very small quantities of gold-bearing ores or concentrates have to be treated. It is used, for example, in Siebenbürgen in the neighbourhood of Abrudbanya, Vöröspatak, Isbita and Kerpenyes, where a small stamp mill and buddle are to be found in every second or third house. The gold-bearing stone is stamped fine and washed on a buddle or on a *sichertrog* (a flat tray, usually of wood, that locally replaces the pan and batea), till it is sufficiently concentrated for amalgamation. It is then rubbed up with mercury in small iron mortars with iron pestles till a plastic paste is formed, in which separate drops of mercury are no longer visible.

The amalgam produced is now separated from the particles of ore and the free mercury by washing; it is then washed several times with hot water, kneaded and made up into little lumps of about 1 lb., each of which is then wrapped in linen and squeezed to remove

excess of mercury. The amalgam thus obtained contains 40 per cent. to 65 per cent. of gold.

This method is not suitable for the treatment of larger quantities of ore or concentrates.

Amalgamation in Rotating Barrels

This method, similar to that described under silver, is but rarely employed, because the mercury is apt to be floured amongst the great quantity of barren rock. It has been used in Brazil, in Spain,[1] and in Siberia.

At Morro Velho in Brazil,[2] ores were crushed in stamps of the old Saxon pattern, with square heads and stems, not rotating. The pulp was concentrated on blanket strakes, and the blanketings amalgamated in barrels. The charge was 17·7 cubic feet of material, containing about 32 ounces of gold, and was treated for 24 hours with 55 lbs. of mercury in revolving barrels. Gold-amalgam containing 50 per cent. of gold was thus produced, the loss of mercury being $\frac{1}{5}$th of the weight of the gold got.

In Siberia,[3] gold-bearing sands are concentrated and amalgamated; the ore is ground, roasted with salt and treated in revolving barrels with mercury, iron filings and sulphuric acid.

Barrels are used in many large stamp mills for amalgamating miscellaneous dirt and scrapings from various parts of the mill.

Amalgamation in Hungarian Mills

Mills of this type, called in Germany "*Quickmills*," are used in Europe, especially in Hungary. The best known are the Schemnitz mill and the recently introduced and very efficient Laszlo amalgamator.

The construction of the Schemnitz mills, which always work in pairs, is shown in Fig. 542. The mill consists of the cast iron pan *g*, inside which works the wooden muller *c*, which is hollowed out like a funnel; the latter is so suspended by the iron arms *r*, *r* as to be free to rotate. The bottom of the muller is furnished with 20 radially disposed iron teeth; it may be driven by a crank as in the figure or by means of gearing. The mercury is poured into the bottom of the pan. The gold-bearing pulp runs from the stamp mill through the trough *a* into the funnel-shaped hollow of the muller; thence it escapes along the bottom of the muller through the space

[1] *Berg und Hüttenm. Ztg.* 1867, p. 212.
[2] *Ibid.*, 1880, p. 93. [3] *Berg-Geist*, 1861. No. 36.

between the muller and the pan bottom, is here forced by the teeth of the muller, which dip into the mercury, into intimate contact with the latter, and finally, passing up through the space between the muller and the pan, escapes through the spout *d*. From this, the pulp passes into a second mill, where the gold is still further extracted. The Hungarian Government owns a big stamp mill at Kerpenyes in Siebenbürgen, with which 128 of these mills are connected. They are charged fortnightly with 26½ lbs. of mercury; the mullers make 30 revolutions per minute.

From the mills the tailings pass over buddles, where the sulphurets are concentrated, and afterwards treated in the dry way.

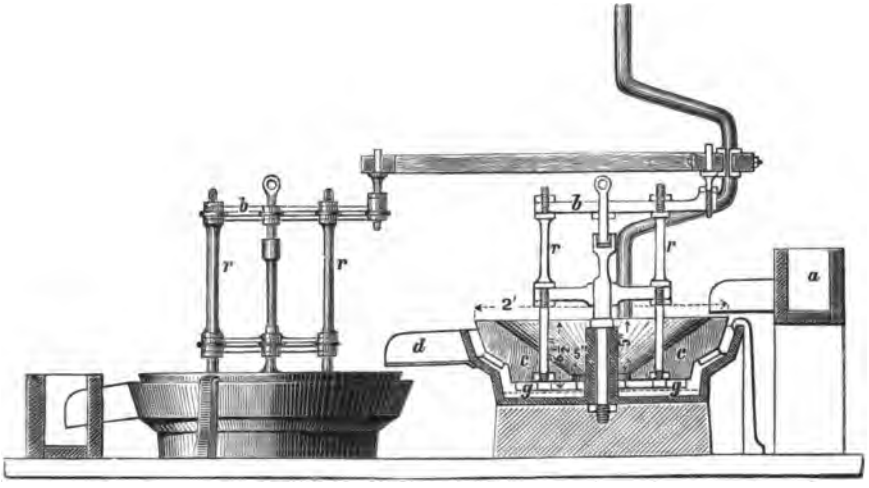


FIG. 542.

In the district of Nagybanya in Hungary, a portion of their gold and silver contents is extracted in similar mills from gold and silver ores after stamping. Each mill is charged with from 40 to 55 lbs. of mercury. After the pulp has traversed two mills one below the other, it passes over buddles of various kinds, to collect the sulphurets contained in it. The average loss of mercury is ½ to 1 part by weight for 1 part of gold-silver alloy. Thus, at the stamp mills at Kreuzberg near Nagybanya, 155 tons of ore were treated in one month, yielding 63 ounces of gold with a loss of 4¼ lbs. (equal weights) of mercury; in another month 754½ tons of ore produced 185 ounces of gold with a loss of 6½ lbs. (½ of the weight) of mercury.

A similar process is in use in the neighbourhood of Schemnitz, where stamped auriferous and argentiferous lead ores with from

2 dwts. 1 gr. to 4 dwts. 6 grs. of gold to the ton, and silver ores with 19 dwts. 14 grs. to 1 oz. 3 dwts. 3 grs. of gold to the ton, are treated in these mills.

The amalgam obtained in these mills is filtered through conical linen bags to remove the excess of mercury and then retorted.

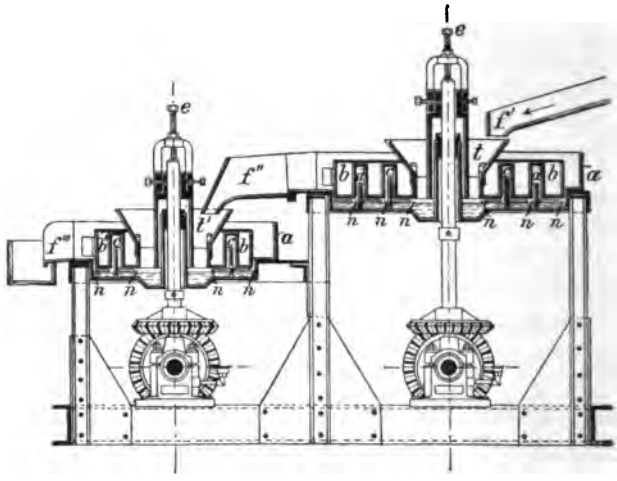


Fig. 543.

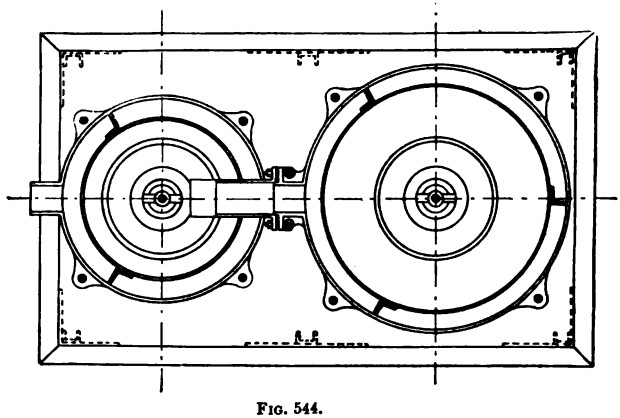


Fig. 544.

The Laszlo amalgamator, which is constructed by the Gruson works at Buckau near Magdeburg, gives a good yield of gold, and is at present in use at Boicza and Ruda in Siebenbürgen. Its construction is shown in Figs. 543 and 544. Here also the mills work in pairs, the lower one serving to complete the amalgamation and to collect the amalgam. The mills consist of a cast iron pan *a* which

is charged with mercury, and a cast iron muller *b*, divided into several annular sections, rotating within it. In the second or smaller mill a loose ring of iron *c* is placed, there being two such, *c* and *d*, in the larger mill. These rings divide the pans into a corresponding number of divisions, and prevent the free escape of particles of gold that are to be amalgamated. The rings are notched at their lower edges in order to enable the mercury to flow freely through the entire pan. The position of the muller *b* can be regulated by means of the set-screw *e*. The pulp coming from the stamps flows through the spout *f* into the funnel *t* of the muller of the first mill, and passes from it into the first division formed by the ring *c*, to do which, it must pass through the space left between the surface of the mercury and the bottom of the muller. It flows over the ring *c* into the second division and thence over the ring *d* into the third division, and finally escapes from the mill through the spout *f''* into the second mill. It here traverses a path similar to that in the first mill, with the difference that it has only to rise over one ring *c*.

The bottom of the muller is furnished with radially-placed iron teeth *n*, which force the particles of gold into intimate contact with the mercury and prevent the accumulation of sulphurets on the latter, which might otherwise block up the machine; on the periphery of the muller there are several such teeth in the form of pieces of angle-iron. The particles of gold are held back by the rings *c* and *d* on account of their high specific gravity, and are thus forced to remain as long as possible in the machine. The speed of the muller depends on the character of the ore that is being treated. Each pair of mills will put through on the average 2 tons of crushed ore in 24 hours. The amalgam is cleaned out at intervals of 10 to 30 days. As examples, the method of gold extraction at the Füzesd Dreifaltigkeit mine near Boicza and at the works of the Twelve Apostles Company of Ruda near Brad, both in Siebenbürgen, may be quoted.

The ores produced at the Füzesd Dreifaltigkeit[1] mine contain both free gold and gold enclosed in pyrites. With the exception of pieces carrying coarse gold, the ores are crushed in Californian stamp mills; each head crushes 0·8 ton in 24 hours. The pulp from each three heads is led to one pair of Laszlo amalgamators. From these they pass into mercury traps and finally are delivered through pointed sizing boxes (*spitzkasten*) to buddles and strakes. The former machine collects auriferous pyrites, which is smelted with lead at Schemnitz; on the latter, sulphurets rich in gold are obtained, which are amalgamated in mortars.

[1] Communicated by the engineer Blumenau.

The upper pan of the amalgamator is 25 inches in diameter, the lower one 22 inches; the latter stands 7 inches below the former. The height of the pans is 4½ inches. The outer ring of the upper pan is 2¾ inches deep, the inner one 4 inches. The ring of the lower pan is 4 inches deep. The outer ring of the muller of the upper pan has 12 teeth on its bottom, the middle ring 8 and the inner one 5. These teeth are made of sheet iron and are 2 inches in length. In the lower pan, which has only two divisions, the teeth of the muller correspond to those of the two inner rings of the upper pan.

The upper pan contains 100 lbs. of mercury in the outer division, and 44 lbs. in the inner one.

The pulp escaping from every three pairs of mills runs into a mercury trap for collecting any particles of amalgam or mercury that may be carried over; it consists, like the amalgamators, of pan and muller, and is only distinguished from them in that it has no teeth.

The power required for 24 pairs of amalgamators and 8 mercury traps amounts to 4 H. P. The output of a pair of mills amounts to 1·7 to 2 tons of ore in 24 hours. The loss of mercury is 0·066 lb. to 0·077 lb. The yield of gold is 75 per cent. to 80 per cent. of the gold present.

The amalgamators are cleaned out from fortnightly to monthly; for this purpose the muller is lifted out of the pan and the amalgam ladled out. Whilst the amalgamator is standing, it is necessary to keep water running through it, to prevent the ore left in it forming a hard crust on the bottom of the pan which can only with difficulty be broken up and treated when the amalgamator is started again.

The ores of the Twelve Apostles Company at Ruda contain on the average 8 dwts. of gold to the ton, including visible gold. The visible gold is picked out in the mine and amalgamated in mortars; the free gold without it amounts to about 4 dwts. of gold to the ton.

The ores are crushed in various stamp mills, one of which is a Californian mill with amalgamated copper plates. The screens have a mesh 0·04 inch wide, but those in the Californian mill only 0·02 inch.

For the Californian mill, which consists of 5 stamps of 750 lbs. weight, 4 pairs of amalgamators are provided; for the other stamps, there is one pair of Laszlo mills for every battery of 3 stamps. These latter stamps are either revolving ones with iron stems or else have wooden stems and weigh 300 lbs. Each head of the Californian stamps crushes 0·6 to 0·8 ton in 24 hours, and of the other stamp mills 1 to 1·7 tons.

Under each pair of Laszlo amalgamators a pair of mercury savers, one below the other, are set. Each amalgamator can put through 3 to 3·5 tons of ore in 24 hours. The consumption of mercury is 0·0028 lb. to 0·0099 lb. to the ton. The yield of gold is 55 per cent.

The tailings are in part treated further in American pans, in part concentrated on buddles and Bilharz tables. The concentrates are smelted with lead at the Schemnitz works.

A new amalgamator, which has not yet been sufficiently tested practically, has been designed by Piccard on somewhat similar principles to the Laszlo amalgamator. It consists of four pans, one below the other, of which the top and third pans revolve, whilst the second and lowest pans are fixed. The upper pan is of wood, the three others of cast iron. The upper pan has sheet iron teeth on its bottom and sides; the two next pans are furnished inside and outside with spiral ribs, whilst the lowest pan has these on the inside only. The pulp is charged into the topmost pan, runs through its centre into the next below, flows over the edge of the latter into the third pan, in the centre of which it rises up a cylinder provided with spiral ribs, through the bottom of which it runs into the lowest pan, over the edges of which it flows away.

This amalgamator is being used at a works at Boicza, but nothing is yet known of its efficiency.

Amalgamation in Pans

This is comparatively rarely practised ; the pans are similar in construction to those employed in the amalgamation of silver ores.

At the Idaho Mill, in Grass Valley, California, the Knox pans, described on p. 665, have been used for treating the sandy skimmings obtained in cleaning the surface of the mercury in the Atwood's amalgamators ; these skimmings contain mercury, amalgam and auriferous sulphurets. The Knox pans are made of cast iron, are 4 feet 2 inches in diameter at the top, 3 feet 11 inches at the bottom, and 14 inches high. The charge consists of 110 to 130 lbs. of impure amalgam to which water and 11 to 16 lbs. of mercury are added. After 3 hours' grinding with the muller down, 4 to 7 lbs. more of mercury are added and a certain quantity of chemicals, such as nitre, salammoniac and sulphate of copper; steam is introduced under the bottom, the muller is slightly raised and run for 3 hours more. Water is then added until the pan is full, and after driving for half an hour, the upper discharge is opened to let the tailings run off. The

tailings are thus run off twice daily. The amalgam is only cleaned up twice a week.

The Boss system of pan amalgamation as described on page 674 is used at the Jay Gould mill at Gould in Montana.[1] The ores consist of a fine grained quartz mixed with clay, in which the proportion of gold to silver is about 1 : 6. The ores are stamped in a Californian stamp mill, and then charged into Boss grinding pans 3 ft. 6 in. in diameter; from these the pulp passes into two larger grinding pans 5 ft. in diameter and 2 ft. 6 in. deep. In 24 hours 10 lbs. of mercury, 220 lbs. of salt (8 lbs. to 16 lbs. to the ton of ore) and a certain amount of lime are added. From these pans the pulp passes to the amalgamating pans with mullers revolving 68 times per minute. After the pulp has passed through 4 amalgamating pans, one below the other, it passes on to the settlers with arms revolving 16 times per minute. After passing through 3 settlers, it goes to the Frue vanners where the sulphurets present are extracted. The loss of mercury is from $\frac{1}{4}$ to $\frac{1}{2}$ lb. to the ton of ore; of the total gold and silver present, 73 per cent. is saved in the pans and 5 per cent. on the Frue vanners.

At the Mysore gold mines, Colar Gold Fields, Mysore, India, a hard quartz is treated by crushing in stamp mills, and the tailings by pan amalgamation. The machinery consists of 90 head of stamps, 55 Wheeler pans and 18 settlers. In 1895,[2] 60,654 tons of quartz were crushed, yielding in the mill 58,855 oz. of gold at the rate of 19 dwts. 10 grs. per ton, and 38,597 tons of tailings were treated in the pans, producing 7,180 oz. of gold, or at the rate of 3 dwts. 17 grs. to the ton.

In many parts of Australia more especially, but also to some extent in other districts, the so-called Berdan pans[3] are used. These consist of a hemispherical bowl of cast iron with a central cone, keyed to a shaft inclined at about 15° and made to revolve at about 25 turns per minute. In the annular space round the central cone are either a couple of heavy cast iron balls or a couple of heavy cast iron drags, shaped to the bottom of the pan. Pulp is fed in at the upper part of the pan, and as the latter revolves, it is ground between it and the balls or drags, and the particles of gold are forced into contact with the mercury that is fed in from time to time. Amalgam thus accumulates in the lowest portion of the pan, whilst the ground tailings are carried off over the lowest part of the edge of the pan by

[1] Egleston, *op. cit.* p. 548.
[2] Directors' Report for the Year 1895.
[3] H. Louis, *op. cit.* p. 343.

a stream of water. This pan is therefore continuous in its action; its average capacity is 2 tons per 24 hours. It requires 1½ I. H. P., to drive it, and needs very little attention, but must have a good continuous water supply.

Amalgamation with the help of Amalgamated Plates

This method has already been described in its most usual form in combination with amalgamation in stamp mills. Cases, however, exist in which inside amalgamation in the mortars is so imperfect that it is altogether dispensed with, and the free gold of the crushed ores is caught only on amalgamated copper tables, whilst the cupriferous pyrites contained in the ore is concentrated on Frue vanners.

Such is the case, for instance, at the Drumlummon Mill at Marysville, Montana; it consists of 60 heads of Californian stamps together with the necessary rock breakers, amalgamated copper tables and Frue vanners. Most of the amalgam is saved on the amalgamated tables and in the sluices lined with amalgamated plates, which carry the slimes to the vanners. A portion is also saved by the Frue vanners and in the sluices with cross riffles placed below the vanners. The tailings retain 20 per cent. of the gold contents of the ore. The concentrates made on the vanners (auriferous and argentiferous iron and copper pyrites) are worth $800 to $1000 to the ton. They are sold to smelting works, where they are treated in the dry way.[1]

A machine that depends upon the use of amalgamated copper plates, but which is only an accessory machine in the treatment of gold ores, is the *Eureka rubber*, formerly used at the Idaho Mill in Grass Valley, California. Its object was to give the *rusty* gold a bright surface, to free the gold from slimy and clayey coatings and to amalgamate the bright gold.

The machine, shown in Fig. 545, consisted of a cast iron box, K in which a system of rubbers moves backwards and forwards. The box has a second bottom consisting of alternate blocks of wood and cast iron plates, *n*, resting on wooden strips at *o*; the rubbing surface accordingly consists of alternate strips of wood and iron. Above it hangs a wooden frame, *h*, in which are secured a number of wooden rubbers, *r*, shod with cast iron. Copper plates are fastened both to the rubbers and the shoes. The height of the rubbing apparatus can be adjusted by means of the rods, *J*, and it is moved to and fro by means

[1] Egleston, *op. cit.* p. 542

of the excentric *Z*, and the connecting rod, *W*, making 55 strokes per minute. There was one Eureka rubber to each 5 head of stamps. The tailings from blanket strakes, as also from special amalgamators (Atwood amalgamators) ran into this machine. The gold contained in them is rubbed bright and remains adhering to the amalgamated copper plates. The tailings from the machine flowed through a row of sluices 2 ft. 6 in. wide, lined with amalgamated plates that saved the rest of the free gold; from these the tailings went to the concentrators.

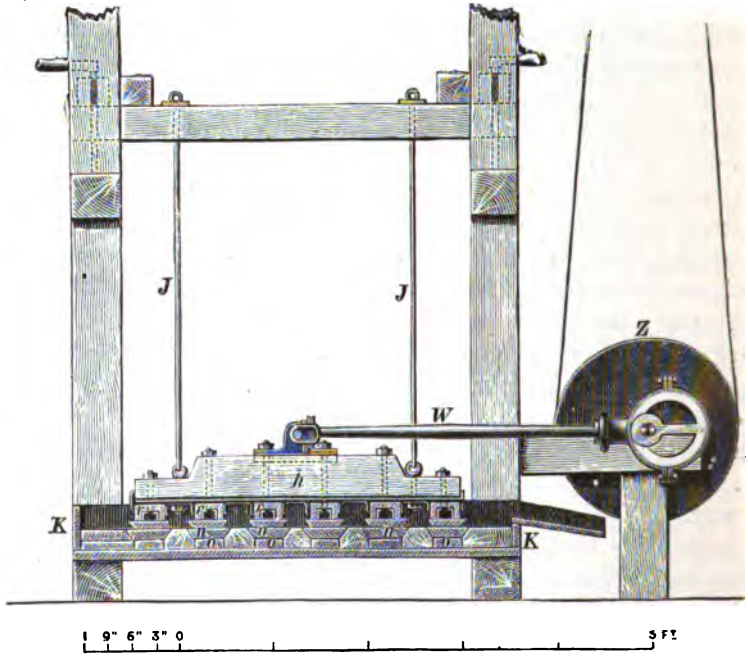


FIG. 545.

Of recent years this machine and this method of working have been abandoned.

Amalgamation in so-called "Amalgamators"

Of other forms of amalgamating apparatus, known by the general term of *amalgamators*, a very large number have been designed; very few of these have ever continued in practical use for any length of time, and modern practice is entirely against their employment. Only a few of the more important will be noticed here.

Atwood's amalgamator was till recently in use at the Idaho Mill, Grass Valley, California. Its construction is shown in Figs. 546 and 547. It consists of an inclined wooden box 4 ft. long, 21 in. wide and 14 in. deep, set at an incline of 3 inches to the foot. In the bottom of it there are two wooden troughs, *t*, 14 inches wide, 6 inches deep and 19 inches long, each of which holds 350 to 400 lbs. of mercury. Above each trough there lies a horizontal rotating cylinder, *c*, 8 inches in diameter and 18 inches long. Iron rods ¼

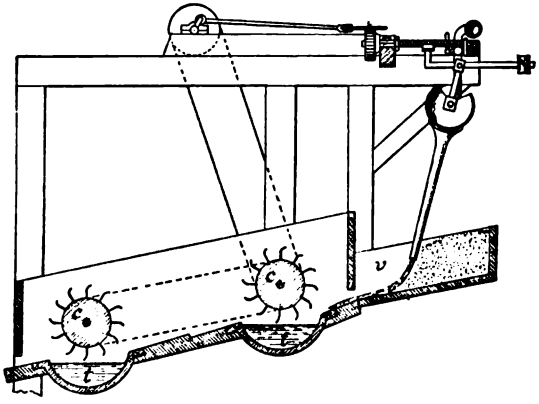


FIG. 546.

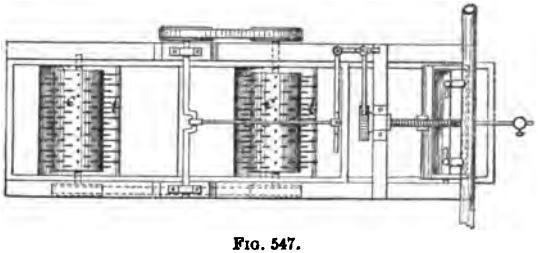


FIG. 547.

inch in diameter and 3 inches long, slightly curved at their ends, are set on the surface of the cylinder at right angles to its axis; these rods reach almost to the surface of the mercury in the troughs. The two cylinders are set 3 feet apart. In the bottom of the box, between the troughs, is a riffle, saw-shaped in cross section, which is filled with mercury. The crushed ore that is to be amalgamated is fed into the charging box, *v*; it is obtained from blanket strakes on which the ore, after being crushed in Californian stamps, is concentrated. By means of a uniformly issuing stream of water from a pipe above it, the ore is carried uniformly through the

amalgamator. The regular flow of water, which is kept at a temperature of 40° to 50°C. is controlled by mechanism placed above the pipe. The rotating cylinders revolve 60 times per minute.

By means of the rods inserted in the cylinder, the lighter parts of the concentrates are kept in suspension, whilst the gold contained in them sinks in the mercury. The lighter portions and the auriferous sulphurets escape with the water at the lower end of the amalgamator, and pass through two sluices containing corrugated amalgamated copper plates to the above described Eureka rubber. A main condition for the effectiveness of the amalgamator is that the surface of the mercury shall be kept constantly bright; as soon as it gets dull it should therefore be brightened by being skimmed. A considerable quantity of skimmings was thus obtained, and these were worked up, as already described, in the Knox pan. The amalgam was cleaned out of the troughs and riffles once a week; the mercury was first ladled out, and then the amalgam carefully removed; 90 to 95 per cent. of the amalgam was saved in the upper trough, the rest in the lower trough and the riffles.

This method of amalgamation, combined with Eureka rubbers and Knox pans, was used for a considerable time at the Idaho Mill, but has recently been abandoned. The ore is gold quartz, whose value according to Egleston for 10 years averaged between $12 and $20 per ton.

These ores were crushed in Californian stamps; the pulp was run through blanket sluices in which lay coarse woollen blankets, in which the heavier portions, gold and sulphurets remained, whilst the lighter portions were taken to the Eureka rubbers. The upper blankets were washed every 10 minutes, the lower every 2 hours, in vats to free them from the heavy particles deposited on them. The blanketings thus saved amounted to 10 to 12 per cent. of the total ore, and were treated as above in the Atwood amalgamators. The tailings from the latter also passed to the Eureka rubbers. The tailings from these passed over amalgamated copper tables, and into Paine and Stevens round buddles followed by tossing tubs, to concentrate the sulphurets. The latter were roasted and chlorinated.

Of the total gold obtained, 65½ per cent. was saved in the amalgamators, 2 per cent. in the riffles, 26 per cent. in the Knox pans, 4½ per cent. in the Eureka rubbers, and 2 per cent. on the amalgamated copper plates of the last sluices. Of the free gold in the ore, 75 per cent. was saved, and 95 per cent. of that in the sulphurets, the latter being worth $80 per ton.

Paul's amalgamator[1] is a trough of galvanised iron with straight sides and cylindrical bottom. It carries a stirrer in the form of a screw covered with amalgamated plates, making 70 to 100 revolutions per minute. The necessary mercury is contained in the bottom of the apparatus.

Crosby's amalgamator[2] is a wooden tub with conical bottom; it is one-third filled with ore, which is stirred up with mercury, the latter being introduced through a rose. When the accumulated mercury reaches a certain level it flows off through an opening in the vessel, and passes through a filter into a bowl covered with leather, which is dipped into a solution of cyanide of potassium; the latter cleans the mercury from grease and dirt, when it again passes into the apparatus. After 4 hours' work the amalgam is separated from the pulp of crushed ore.

The author is not aware that either of these machines have found any practical application.

Various amalgamators have been founded on the principle of allowing auriferous ores to ascend through a column of mercury; among these may be named those of Ball,[3] Tichenor[4] and Stevenot,[5] none of which have, however, been applied practically. An apparatus of Thenot based on this principle, but also untried, consists of a series of cast-iron pots, of which the lower part of the hinder one always communicates with the upper part of the one in front by means of a pipe. The pots are filled with mercury up to a given level. By the pressure of a column of water or of ore pulp the latter is forced through the mercury in the various pots, one after another. The regulation of the pressure is effected by means of a valve on the escape pipe from the last pot.

Among these devices, the mercury well, used in all parts of the world, and at one time very largely in Australia, must be included. It consists of a shallow rectangular trough of cast iron or wood, a few inches wide and deep, and of the full width of the battery lip. It is divided at right angles to the flow of the pulp, that is, parallel with its longer side, by an adjustable baffle board, that does not reach quite to the bottom. It is filled with mercury to just above the bottom edge of the baffle board, so that the pulp streaming through has to come into contact with the mercury. The amalgam formed collects in the bottom of the well, which is cleaned out at intervals. Usually several of these wells (2 to 5) are placed one immediately

[1] *Berg-. und Hüttenm. Zeits.* 1872, pp. 55, 382; 1875, p. 91; 1878, p. 314.
[2] *Ibid.* 1874, p. 12; 1875, p. 275.
[3] Imperial German Patents, No. 8306.
[4] Do. No. 11,294.
[5] *Oester. Zeitsch.* 1879 p. 248.

below the other, to be often followed in modern practice by amalgamated copper plates.

Numerous amalgamators on the centrifugal principle have been invented, *e.g.*, that of W. A. Howard,[1] of Brisbane, Queensland, and many others.

The Designolle Process of Amalgamation

This has been found as little suitable for the extraction of gold as for that of silver (see page 702).

THE TREATMENT OF GOLD AMALGAM

This is identical with the treatment of silver amalgam. The amalgam is usually clean enough to be distilled or *retorted* as soon as the excess of mercury has been filtered off. Amalgam off the plates is usually so stiff that it can be at once kneaded into balls with the admixture of a little mercury. Very impure amalgam is treated in the United States like impure silver amalgam, in Knox pans or in revolving cast-iron barrels. It is then washed in pans with mercury and filtered.

This amalgam is then retorted like silver amalgam. In the United States, Africa, &c., horizontal cylinders of cast iron as well as pot-shaped retorts are used.

Cylindrical retorts have been described under the head of silver (see page 705). They are 3 feet to 4 feet long and 12 inches in diameter. The retorts and condensers are arranged as for silver. The charge varies from 200 to 1,200 lbs. of amalgam. The heat is slowly raised up to the boiling point of mercury and maintained for 2 hours at that temperature; it is then raised to dull redness, at which it is maintained for an hour. The retort is then allowed to cool for 4 to 6 hours, when the gold is withdrawn. To retort 1,000 lbs. of amalgam $\frac{1}{8}$ to $\frac{1}{2}$ cord of wood is required.

A retort lasts for 100 to 300 charges. The loss of mercury is very small, amounting to 1 to $2\frac{1}{2}$ lbs. of mercury to the ton of amalgam. The gold sponge so obtained is 600 to 850 fine in California. It is melted in retorts with nitre and carbonate of soda.

In the smaller mills of the United States and elsewhere, pot retorts of the shape shown in Fig. 548 are used. They are made of cast iron, turned on their upper edge; the lower edge of the cover is also turned to match. Their sizes vary greatly, from a capacity of 150 oz. to 2,000 oz. The largest, for 2,000 oz., are 8 inches in

[1] Patent, December 17, 1892.

diameter at the top, 6 inches at the bottom, and 12 inches high; the smallest size, for 150 oz., is $3\frac{7}{8}$ inches diameter at the top, $3\frac{1}{8}$ inches diameter at the bottom, and $4\frac{1}{2}$ inches high.

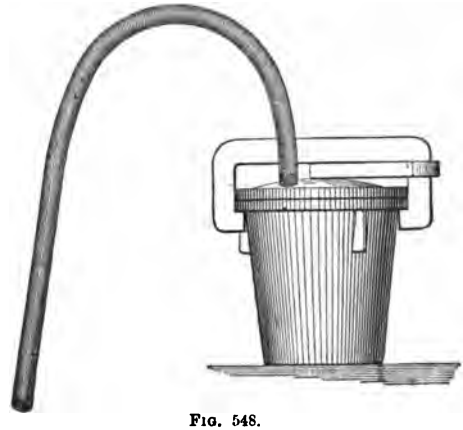


FIG. 548.

A retort used in Hungary is shown in Fig. 549. It is a vertical cylinder of $8\frac{3}{8}$ inches inside diameter and $14\frac{1}{2}$ inches high, standing on a grate, *b*, and narrowed down at the bottom to a collar $2\frac{3}{4}$ inches in diameter, into which the tube *c* fits. The furnace, *R*, is 4 feet 3 inches high and 1 foot 8 inches in diameter, and is closed above by a cast-iron plate. The amalgam to be retorted is laid on sheet-iron plates, *t*, that are threaded on to the iron rod, *m*. A bell-shaped cover *D*, closes the upper end of the retort. The fuel (charcoal) is heaped up round the retort in the body *r*, of the furnace, the products of combustion escaping by the stack, *g*. The mercurial vapours pass through the pipe *c*, into the cast-iron tube *d*, which is $6\frac{3}{4}$ inches wide and is closed above by a plug *e*, and they condense in the box *h*, filled with water. The operation of retorting takes 4 hours.

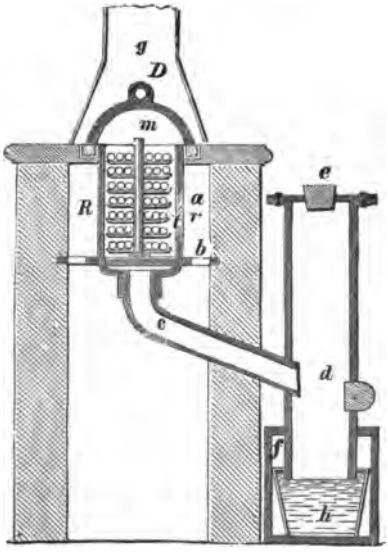


FIG. 549.

B. THE EXTRACTION OF GOLD BY MEANS OF AQUEOUS SOLUTIONS

Up to the present there are two methods in use by which gold may be dissolved out of ores properly so-called, and got in the form of an aqueous solution, to be subsequently precipitated as metal, namely that by which the gold is obtained in solution as a chloride, and that by which it is obtained as potassic aurocyanide. These processes are known as

the Plattner process and the MacArthur-Forrest process, after their respective inventors.

The method of dissolving gold as a hyposulphite by means of sodic, calcic or cupro-sodic hyposulphite is only used for silver ores that contain comparatively little gold. In this case double salts of gold, *e.g.*, $3Na_2S_2O_3$, $Au_2S_2O_8 + 4H_2O$, are produced.

The Plattner process may be used in many cases in which amalgamation fails, especially on pyritic ores. The MacArthur-Forrest process, which is only a few years old, is, according to experience hitherto, best suited to ores that are *free-milling, i.e.*, that will yield gold to mercury, but contain the gold in a fine state of division. It is also applicable to pyritic ores, but is then not as advantageous as the Plattner process. There are, however, gold ores, on which neither amalgamation, chlorination nor cyanidation yield satisfactory results, so that there is here a wide field open to metallurgical research.

THE PLATTNER PROCESS

This process depends on the action of chlorine gas upon moistened gold ores, leaching out the so formed auric chloride with water, and precipitating metallic gold from the solution of its chlori de by ferrous sulphate, charcoal, sulphuretted hydrogen or sulphides.

It was proposed in 1848 by Plattner for the extraction of gold from the arsenical pyrites residues of the works at Reichenstein in Silesia, and was introduced in 1858 by Deetken, at Grass Valley, California. Since 1863 it has attained great importance in the gold mining States of the Union, and has been modified there in many ways as regards the form of the plant and the method of generating the chlorine. From America it was introduced into Australia and South Africa. It is also in operation in Austro-Hungary.

Many ores from which mercury will not extract gold can be advantageously treated by the Plattner process; amongst these more especially are pyritic ores containing gold in a very fine state of division. But there are also many ores, also pyritic, from which chlorine will not extract the gold perfectly.

The conditions for the satisfactory chlorination of gold ores are the absence of bodies attacked by chlorine, a fine state of division of the gold, the absence of bodies that coat the particles of gold and protect them against the action of the chlorine, and the employment of pure chlorine, more especially free from hydrochloric acid.

As chlorine attacks arsenides, antimonides and sulphides, ores that contain these substances must be subjected to an oxidising calcination before being chlorinated, so as to remove antimony,

arsenic and sulphur, and to convert the metals into oxides. In this calcination a small percentage of salt is generally added, in order to convert any substances that might be present and which would form chlorides on chlorination into chlorides during the operation of roasting, so as to save chlorine during chlorination.

Many ores are also roasted before chlorination, in order to make them more open in texture, and thus render the particles of gold accessible to the action of chlorine.

Any silver present in the ore forms chloride, which coats the particles of gold, and thus renders their chlorination more difficult. The process therefore gives better results in the absence of silver. Any sintering of the ore during calcination is also apt to cover up particles of gold and to prevent their being chlorinated; all sintering must therefore be avoided in calcining the ore.

If the gold is not very finely divided, its chlorination takes too much time, hence ores carrying coarse gold are not adapted to this process.

If the chlorine gas contains hydrochloric acid, the latter will attack any sulphides that may be left, and generate sulphuretted hydrogen, which would precipitate as sulphide any gold in solution as chloride, and thus render it insoluble. Hydrochloric acid would also dissolve metallic oxides.

The chlorine employed in this process is produced either from black oxide of manganese, salt and sulphuric acid, or from chloride of lime and sulphuric acid. In the former case it is produced in special generators, in the latter inside the chlorinating vessel itself. Pressure has been used in chlorinating, but it has not given results notably superior to those obtained without pressure.

The apparatus in which the gold is chlorinated, when working on a very small scale as formerly at Reichenstein, and now at times at Freiberg, consists of vessels of glazed earthenware, but on a large scale, as for instance in the United States and Australia, of vats of tarred wood with double bottoms, or lead-lined rotating wooden or iron barrels.

The Plattner process is most extensively used in California; in the ores there the greater portion of the gold is *free-milling*, or exists in such a form that it can be extracted by amalgamation, whilst another portion is enclosed in sulphurets (iron, copper and arsenical pyrites) in such a form as not to be affected by mercury; this latter portion is chlorinated. After the ores have been treated as already explained by inside and outside amalgamation, the tailings are concentrated on Frue vanners to extract the sulphurets, and the concentrates so obtained are treated by the Plattner process.

These sulphurets generally amount to 1½ per cent. to 2 per cent. of the ore, and only exceptionally reach 7 per cent. to 10 per cent.; their average value may be taken as $40 to $100 per ton.

The composition of such concentrates is as follows :—

	I Eureka and Idaho Mines, Grass Valley.	II Washington Mine, Mariposa County.	III Black Bear Mine, Klamath County.
Cu	0·85	—	—
Pb	0·78	1·50	—
Au	0·02743	0·00914	0·0137
Ag	0·0068	0·0035	0·0030
Zn	—	1·34	—
Fe	40·65	30·85	42·05
As	trace	—	21·25
S	32·80	31·33	25·10
Si	12·64	33·30	10·35
Al	0·10	—	0·85
Mg	3·50	—	—
O and loss	8·65	1·67	0·38

The Plattner process is more rarely applied to ores direct, that is to say without previous concentration or amalgamation, as for instance at Mount Morgan in Queensland and Black Hills in Dakota.

In the execution of the process we have to consider :—

1. Calcining the ore.

2. Chlorinating the gold and leaching the auric chloride out of the ore.

3. Extracting the gold from the solution of its chloride.

If the gold ores contain silver, the chloride of silver, being insoluble in chlorine, remains in the residues. In this case after the gold has been removed, the residues are leached with hyposulphites.

CALCINATION OF THE ORES

The object of calcination is to liberate the gold and to convert all metals present, except gold and silver, into oxides, which are but little attacked by chlorine. In many cases, *e.g.*, when gold is contained in brown haematites, the object of the calcination is merely to render the gold readily accessible by expelling water and rendering the ground ore porous.

Arsenic, antimony and sulphur must be removed as completely as possible by the calcination; soluble salts, such as ferrous sulphate or chloride, may not be left in the calcined ore, because they would precipitate gold from the solution of its chloride. Lime and magnesia are injurious inasmuch as they absorb chlorine during

chlorination, and thus increase the chlorine consumption. Lead also absorbs chlorine.

When the ores contain lime, magnesia or lead, salt is added towards the termination of the roasting, so as to convert these metals into chlorides, in order to prevent free chlorine acting on them during chlorination. Lead is partly converted into sulphate on roasting, and this salt reacts with sodic chloride, forming sodic sulphate and lead chloride, or in the presence of oxide of lead, lead oxy-chloride, otherwise lead would be converted into oxy-chloride by the free chlorine.

When salt is added the temperature must be kept down to prevent the volatilisation of any gold chloride that may be formed. If copper is present in the ore, the chloride of copper powerfully promotes the volatility of the gold. The salt must then only be added when all the copper has been converted into oxide.

According to Stetefeldt [1] the loss of gold by volatilisation as chloride during a chloridising roast may equal from 40 per cent. to 90 per cent. of the total gold present, according to the degree of temperature and the length of time occupied by the calcination. The above writer's experiments show that when cupriferous gold ores were roasted with only 3 per cent. of salt, the following results were obtained :—

No. of the charge.	Gold contents.		Loss of Gold per cent.
	Before the chloridising roast.	After the chloridising roast.	
	In a reverberatory furnace.		
2	0·916	0·426	53·5
4	0·262	0·150	42·8
5	0·538	0·075	86·1
6	0·650	0·075	88·5
	In a muffle furnace.		
1	0·700	0·050	93·0
2	0·525	0·075	85·7
3	0·650	0·065	90·0

According to S. B. Christy, gold is but slightly volatile [2] in an atmosphere of chlorine gas at 100° C.; its volatility increases slightly up to 250° C., and then diminishes till below redness, commences to increase again at a red heat, and rises continually up to white heat.

If the ores contain silver, the addition of salt will convert it into chloride, which is extracted by means of hyposulphite solution. If

[1] *Trans. Amer. Inst. Min. Eng.*, vol. xiv., p. 336.
[2] *Ibid.* vol. xvii., p. 26.

the chloride of silver covers up particles of gold, it is best to leach before and after chlorination, otherwise only after the chloride of gold has been dissolved out. If the calcined ore contains much chloride of lead, it is best removed before chlorination by leaching with hot water.

The quantity of salt to be added, the time required for calcination, and the temperature to be maintained, so as to ensure the minimum loss of gold, have to be determined experimentally for each individual kind of ore.

The appliances used for calcination are reverberatory furnaces of the most varying kinds, continuous acting furnaces with one bed, with several beds one over the other, with several beds arranged stepwise, with elliptical beds, as also rotating cylinders, and finally Spence furnaces.

The best form of furnaces with fixed beds are the continuous reverberatories with one bed, and working doors on either side, as also those with stepped beds, the latter being much used in California.

Furnaces with elliptical beds, such as are also used in California, are difficult to construct and are unable to show any corresponding advantage over the rectangular bed.

When large quantities of ore have to be put through, rotating cylinders, improved O'Hara furnaces and Spence furnaces may be recommended.

Continuous-acting reverberatory furnaces are best made 55 feet to 66 feet long; such a furnace will put through on the average 3 tons of ore in the 24 hours.

At the Treadwell Mine[1] in Alaska the pyrites are calcined in a Spence furnace with 4 shelves; the crushed concentrates, which contain $40 to $50 in gold, are mixed with 3 per cent. of salt on the third hearth. They remain 16 hours in the furnace, which roasts 8 tons in 24 hours.

At the works at Sutter Creek, Amador County, California,[2] a long-bedded calcining furnace (*Fortschaufelungsofen*), 80 feet long and 12 feet wide, is used. The ore is charged in lots of $1\frac{1}{4}$ to $1\frac{1}{2}$ tons; each furnace takes 3 charges at a time, which are worked and drawn separately. In 24 hours, 3 charges, weighing together $3\frac{3}{4}$ to $4\frac{1}{2}$ tons, are put through. The charge nearest the flue is being dried, whilst the middle one is being freed from the greater part of its sulphur, and the one nearest the fire bridge is being roasted dead. The salt ($\frac{3}{4}$ per cent. of the charge) is added as soon as no more sulphur flames appear.

[1] Egleston, *op. cit.*, p. 606.

[2] *Ibid.*, p. 607.

At the Amador Reduction Works, near Amador City, California, long-bedded calciners, 75 feet long and 12 feet wide inside, with 6 working doors on either side, are used. In 24 hours, 3 tons of ore are roasted with a fuel consumption of 1 cwt. of wood. Salt amounting to 1 per cent. of the weight of the charge is added. Only one man is required per 8 hour shift.

At the Eureka Works in Grass Valley, California, there was formerly a *fortschaufelungs* furnace with 2 hearths, one above the other, of which the upper one was 39 feet long and 6 feet wide ; the lower hearth was as wide, but much shorter. Of the crushed ore, 9 tons were always on the upper hearth and only 1 ton on the lower. After the lower hearth was emptied, 1 ton was pushed down from the upper hearth and spread out, and 1 ton of fresh ore charged on to the upper hearth. In 24 hours 3 tons were calcined ; the furnace required 2 men to the 8 hour shift.

At the Providence Works, near Nevada City, in California, furnaces with 2 elliptical hearths one above the other, are in use ; the longer axis of the hearths is 15 feet, the shorter 12 feet. The ore, which contains $120 in gold and $12 in silver per ton, is first dried in 5 ton charges on the roof of the upper bed, and is then dropped through openings on to the bed, where it is spread out and rabbled every 10 or 15 minutes. Every 12 hours, 2 tons are passed from the upper to the lower bed through openings in the former, and is replaced by a similar quantity of dried ore. After the ore has been 4 hours on the lower hearth, the temperature is reduced and 1 per cent. of salt is rabbled into the ore ; the temperature is raised and rabbling is continued for 4 hours more, when the charge is drawn.

At the Deloro Mine, Ontario,[1] Canada, the ore is dried in a revolving cylinder, and then roasted in 2 revolving cylinders placed one above the other ; the upper one is 30 feet long and 5 feet in diameter, and its lower end communicates by means of a pipe with the lower cylinder, which is 20 feet long and 4 feet in diameter. The products of combustion traverse first the lower and then the upper cylinder, the ore travelling in the opposite direction. Ten tons of ore are calcined in 24 hours.

As already stated, the calcination takes place at a low temperature, which is only raised at the finish in order to decompose the sulphates formed as far as possible.

After the ore has been drawn from the furnace, it is first piled up in heaps to produce an after-chlorination, and then spread out on a

[1] *Trans. Amer. Inst. Min. Eng.*, vol. xi., p. 193.

cooling floor. When completely cool it is moistened with 4 per cent. to 5 per cent. of water and chlorinated. In case of need the soluble salts and the chloride of silver are leached out before chlorination.

Chlorination of the Gold and Leaching out the Chloride of Gold

Chlorination is effected either with the ore at rest in fixed vessels or in vessels suspended on trunnions, or with the ore kept in a state of agitation in rotating vessels, usually cylindrical.

The chlorine can either be generated in separate producers, washed and passed into the ore, or may be generated inside the chlorination vessels by adding to the ore reagents capable of evolving chlorine. In closed rotating vessels chlorination can be performed under pressure, which is not possible in open vessels or vats.

Chlorination in rotating vessels is more rapid than in vessels where the ore is at rest, and will extract a higher proportion of gold. By the movement of the ore the particles are broken up and thus the separate particles of gold better exposed to the action of the chlorine; any coating on the gold is also apt to be removed by the friction of the particles of ore against each other. Chlorination proceeds especially well when the chlorine is generated in the revolving vessels themselves from chloride of lime and sulphuric acid, as it has a powerful chloridising action on the gold in the nascent state, and is brought into intimate contact with the particles of the gold owing to the rotation of the vessels.

The application of pressure favours the chlorination of the gold but has not produced all the advantages that were expected of it. Accordingly it is nowhere in use at present, as far as it includes these methods, in which chlorine was forced into the chlorination vessel by artificial pressure.

Sutton has proposed to chlorinate in an iron vessel lined with lead and provided with two stirrers.

Chlorination without Agitation of the Ore

(a.) When Chlorine is generated outside the Chlorinating Vessel

In this process the vessels used on a small scale are made of stone ware, on a large scale of tarred planks.

At Reichenstein in Silesia, where the Plattner process was introduced, stoneware vessels were used. Calcined arsenical pyrites containing 0·0022 per cent. to 0·0024 per cent. of gold, the residues from arsenic manufacture, were there submitted to chlorination. The vessels were stoneware cylinders 24¾ inches high and 16½ inches

in diameter, terminating in a cone below, iron hooped, and hung on trunnions. Inside each was a filter composed of pieces of quartz resting on a perforated tile. The vessel was closed air-tight by means of a wooden cover that was luted on; through it a leaden tube reached nearly to the bottom of the vessel and served for the introduction of the chlorine. The charge of ore amounted to 165 lbs.

The chlorine generator was of stoneware and was provided with a leaden cover luted on by means of dough. It was heated on a sand bath. There were two openings in the cover; one for the introduction of the necessary chemicals, the other provided with a leaden tube, through which the chlorine was led to the wash-bottle. The generator was charged with 16½ lbs. of hydrochloric acid, 7¾ lbs. of dilute sulphuric acid (25° B.) and 7¾ lbs. of black oxide of manganese. The chlorine gas was first washed in the wash-bottle to remove hydrochloric acid, and then led through the bottom of the chlorination vessel under the slightly moistened ore; after 6 or 7 hours the chlorine gas was shut off. The vessel was then allowed to stand another 12 to 15 hours, so as to admit of the complete absorption of the chlorine, and the chloride of gold was then dissolved out with water at 20° C., until the ore was exhausted. An objection to the process arose from the fact that these residues absorbed large quantities of water, so that the complete washing out of the dissolved gold was a matter of great difficulty.

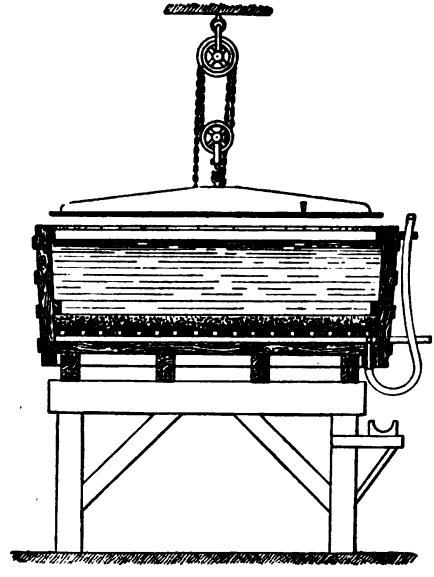


FIG. 550.

In Freiberg imported gold ores are at present treated by the Plattner process in stoneware vessels.

Wooden vats, such as are used for operations on a large scale, are either fixed or suspended on trunnions. They receive inside and out 3 coats of tar, asphalt varnish or paraffin, which renders them both proof against chlorine and impervious to liquids.

Fixed vats are cylindrical, 5 to 9 feet in diameter and 2 feet 6 inches to 3 feet deep, inside measurements. According to their size

they will take 2 to 5 tons of ore. Some distance (about 1½ inch) above the true bottom is a false bottom of perforated planks, upon which there is a layer of pieces of quartz 6 to 8 inches deep; at the bottom these pieces are of the size of hens' eggs and gradually decrease in size towards the top of the layer; upon it there is a layer of sand 2 inches deep; upon this a filter of sailcloth is laid, which is sometimes replaced by a layer of wooden boards. The construction of such a vat is shown in Fig. 550. Chlorine is led in through the horizontal pipe; the solution is run off through the bent up hose-pipe.

The dimensions of some of these vats and their capacities are shown in the following table:[1]—

Name of Works.	Diameter.	Depth.	Capacity.
	Feet. in.	Feet. in.	Tons.
Treadwell Mine, Alaska	9 –	3 –	5
Amador Mine, California	8 6	3 6	3½
Plymouth Mine, California	9 –	3 –	4
Sierra Buttes Mine, California . . .	5 –	3 2	2
Caillots Mine, California	8 –	3 6	3
Providence Mine, California . . .	6 –	2 6	3
Maltmans Mine, California	5 –	4 –	2

The arrangement of a vat suspended on trunnions is shown in Fig. 551; *a* are the trunnions, and *b* is a perforated stoneware slab, below which there are fragments of quartz. Chlorine gas is passed in through a lead tube beneath the false bottom, provided with a tap. Such vats are in use at Grass Valley, California. They are 3 feet 3 inches high, 5 feet in diameter at the centre and hold 3 tons of ore.

The ore to be charged must be moistened to the right degree; ore that is too dry is not sufficiently attacked by chlorine, whilst ore that is too moist prevents the chlorine gas from rising. As soon as the vat has been filled a foot high, chlorine is passed into the space between the double bottoms, whilst the charging continues until the vat is filled with ore up to 2 inches to 4 inches from the top. It is then closed with a cover in which there are holes to allow the air to escape and the gases to be observed. The cover is luted down by means of a clay puddle, which is kept moist by being covered with wet rags. Chlorine is allowed to enter the vat for 5 to 12 hours, according to the fineness of the gold; the admission pipe is then closed and the vat is allowed to stand for 24 to 40 hours with the cover on.

The finer the gold, the more rapidly does it chlorinate.

[1] Egleston, *op. cit.*, p. 628.

The chlorine is generally produced from black oxide of manganese, salt and sulphuric acid. The chlorine generator is a vessel of heavy sheet lead or of iron, lead-lined, with a water-sealed cover. Its construction is shown in Fig. 552. Its dimensions (for chlorinating a 3 ton charge) are 20 to 24 inches in diameter and 12 inches in depth. The solid chemicals are charged in by lifting off the cover; the fluids are added through the doubly bent tube *a*. The apparatus stands on a sandbath, by which it is raised to the temperature of 50° C., which is the best for chlorine generation, and is fitted with a wooden stirrer which is turned by hand from time to time. The wooden shaft of the stirrer passes through a hydraulic seal, and is lifted during the time it is not in use. The sandbath

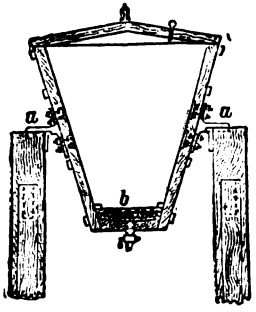


FIG. 551.

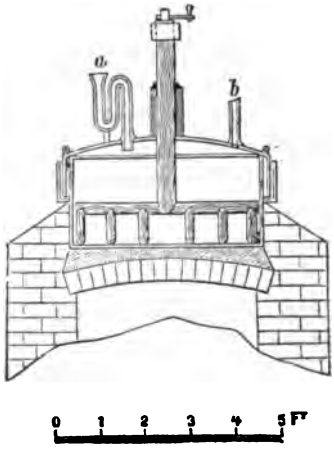


FIG. 552.

rests on a brick arch, which stands above a firegrate. Water- and steam-baths are preferable to the sand-bath, because they produce a uniform temperature and thus prevent the formation of hard crusts in the generator; this makes it possible to dispense with the stirrer. Through the tube *b* the chlorine gas is led into the wash bottle by means of an india-rubber pipe.

More recently the hydraulic seal to the cover has been done away with at some works, and the cover is then luted tight to the generator by means of dough.

For the chlorination of 3 tons of ore, the charge consists of 20 lbs. to 24 lbs. of salt, 15 lbs. to 20 lbs. of binoxide of manganese, 30 lbs. to 45 lbs. of sulphuric acid of 66° B., and 18 lbs. to 25 lbs. of water

When the charge has remained 48 hours, on the average, in the

vats, the chloride of gold is leached out with water. For this purpose the cover is removed, the ore is covered with sacking and water is run on to the latter, by which means the water is uniformly distributed throughout the ore. In many works the sacking is put over the ore before the cover is put on, and water is run in through holes in the closed cover. As soon as the water stands 3 inches above the surface of the ore, and no longer settles into it, it is allowed to flow off. The solution of chloride of gold is allowed to escape through an opening in the true vat bottom, and water is run in at the top as fast as the gold chloride solution flows out, so that the water level in the vat remains constant. The water is not cut off until the escaping solution no longer shows any gold reaction.

The solution of chloride of gold is run out through an indiarubber pipe, the bent up hose (shown in Fig. 550) being let down when the solution is to be run off. It runs through a wooden launder into wooden settling vats, or into filtering bags, and finally to the precipitating vats. The mechanical impurities of the solution are retained on the filters or in the settling vats; any lead present is also retained the soluble chloride of lead being converted into insoluble sulphate by the sulphates present.

The composition[1] of a clear solution of gold chloride from chlorinating a 3-ton charge of ore, yielding $163 to the ton, is given by Deetken as follows, the sample being taken 1 minute after the discharge cock was opened :—

Aluminium sulphate	6·98	grains
Magnesium sulphate	132·55	,,
Lead sulphate	4·16	,,
Sodium sulphate	426·62	,,
Gold chloride	10·44	,,
Ferric chloride	0·32	,,
Cupric chloride	8·95	,,
Sodium chloride	536·00	,,
Silica	0·24	,,
Free chlorine by difference	101·02	,,
	1227·28	,,

The leached and washed ore is shovelled into special vats for leaching out the silver when it contains any; otherwise it is removed as barren tailings.

The leaching of the chloride of silver from the residues of gold

[1] Egleston, *op. cit.* p. 642.

chlorination is performed by means of sodic or calcic hyposulphite as described under silver. The silver is precipitated from the solution as sulphide by sodic or calcic sulphide.

For example, at the Sierra Buttes Mine, California, the ore after it is freed from chloride of gold, is leached for 48 hours in vats 5 feet high and 3 feet 6 inches in diameter, with a 3 per cent. solution of sodic hyposulphite, the solution being afterwards precipitated with sodic sulphide. The precipitate of silver sulphide thus formed is roasted and sold. The solution vats at the Providence Works, California, are 6 feet 6 inches high by 3 feet 6 inches in diameter, and at Meredith's Works are 6 feet in diameter and 3 feet 3 inches high.

(*b*) *Chlorination without Agitation of the Ore, when Chlorine is Generated inside the Chlorination Vat*

This method, devised by the Swedish engineer Munktell, and known as the Munktell process, consists in charging the ores, which if necessary are first submitted to a chloridising roast, into vats, and allowing dilute solutions of calcic hypochlorite and of an acid, which are allowed to mix immediately above the layer of ore, to percolate slowly through the latter. By the union of these reagents chlorine is evolved, which converts the gold into chloride, the salt being dissolved by the liquid. The latter escapes from the vats free from chlorine and the gold is precipitated out of it, as will be presently explained. The solution of calcic hypochlorite must not contain over 1 per cent., and the acid which acts on it must be so dilute that the volumes of the two solutions shall be equal.

In a well arranged plant two small vats are disposed over the leaching vat, to be filled respectively with calcium hypochlorite solution and acid. These vats deliver into two launders that meet above the main vat. After these small vats have been filled and the supply pipes are closed, equal quantities of the two solutions can be allowed to run out together.

This process, which was recently used at Kolm Saigurn in the Salzburg Alps, and is still in operation at Brad, in Siebenbürgen, is inferior to the process on similar principles conducted in revolving barrels (Miers and Thies processes).

Chlorination with Agitation of the Ore

This method has hitherto only been carried out in rotating barrels. (Sutton proposed fixed vessels provided with two stirrers, which were tried experimentally at Mount Morgan, Queensland; no

statements as to their efficiency have as yet been forthcoming.) High pressures have been employed in this method, but have been again abandoned.

Mears produced such pressure, both by the employment of considerable quantities of chloride of lime and sulphuric acid in the chlorinating vessel, and by forcing in chlorine which was generated in separate apparatus outside the chlorinating vessels. Newbery and Vautin employed liquid chlorine generated inside the chlorinating vessel. Both methods have been abandoned, since it has been shown that chlorination proceeds equally well at low pressures. Pollock's method, too, of employing hydrostatic pressure, never appears to have come into regular use. The universal practice now is to generate the chlorine in the chlorinating vessel, as in the methods of Thies and Davis, from chloride of lime and sulphuric acid; the chemicals are charged by small quantities at a time, so that no high pressures, capable of rapidly damaging the lead lining, can be produced.

Mears's process was used, for example, at Deloro, in Canada; the ores, calcined arsenical pyrites, carried $79 to $90 gold per ton. The rotating barrels contained 1 to 3 tons of ore. The chlorine was first generated in these barrels from chloride of lime and sulphuric acid, which substances were charged in large excess, but it was afterwards found preferable to generate the chlorine outside the barrels from salt, oxide of manganese and sulphuric acid, and to force it in through a hollow axis of the barrel. The pressure in either case was 30 to 40 lbs. to the square inch, and the time occupied in chlorination was 2 to 2½ hours. The chief disadvantage of the process lay in the lead lining becoming leaky, and in the difficulty of repairing the same.

The Newbery-Vautin process was used for a time at Mount Morgan, Queensland. It consists in the use of liquid chlorine for chlorinating, and in leaching the chloride of gold out of the ores under a partial vacuum. Chlorine was supposed to act very rapidly and energetically in the liquid state, whilst the vacuum pump made rapid leaching and filtration possible. The latter point was considered especially important in the case of tenacious and slimy ores on which the ordinary Plattner process could not be employed, on account of the difficulty of washing and filtering. The chlorinating vessel was a horizontal rotating barrel, made of iron and lined with lead. The chlorine was generated in the cylinder from chloride of lime and sulphuric acid. Compressed air at a pressure of 4 atmospheres was forced in, which liquefied the chlorine in the barrel previously charged with ore; the barrel was then caused to rotate,

and the chlorination of the particles of gold was completed in from 1 to 4 hours, according to their size. The air was then allowed to escape together with the chlorine, which again assumed the gaseous form under the diminished pressure, and passed through a vat containing lime-water, in which the chlorine was retained. The contents of the chlorinating barrel were then emptied into a leaching vessel provided with a filter and suspended on trunnions, which was placed below the barrel. A vacuum pump was applied below the filter, so that filtration and washing could be performed rapidly. The solution was passed through a filter of charcoal on which the gold was precipitated.

This process has been abandoned and replaced by chlorination in wooden lead-lined barrels, in which the chlorine is generated from chloride of lime and sulphuric acid.

Chlorination in horizontal rotating barrels at low pressure is nowadays employed by preference, as it works nearly as well as under high pressure, and possesses the advantage that the leaden lining of the barrels is but little attacked. The chlorine is best generated inside the chlorinating vessel, as it acts more energetically in the nascent state than when it is led in from the outside.

This method, known in the United States as the Thies process, is, *e.g.*, used at the Bunker Hill Mine near Amador City, California, at the Phœnix and Haile Mines in North Carolina, in the Black Hills, Dakota, and the Mount Morgan Mine, Queensland. The barrels are made of cast iron, wrought iron, or more rarely of wood as at Mount Morgan. Cast iron is generally employed. The sheet lead, with which the barrels are lined, is 0·25 inch in thickness, and is bolted to the sides of the barrels. In America the outside diameter is 4 feet, the inside 3 ft. 4 in.; the length over all is 6 feet, and in the clear 4 ft. 6 in. Ribs were at one time used inside the barrel to raise the ores and allow them to fall again as the barrel revolved, but have been removed because chlorination was not improved by them. The heads of the barrels are always of cast iron, provided with trunnions cast in one piece with them. Each barrel holds 1 ton of ore.

The necessary quantity of water (135 to 140 gallons of water to the ton of ore) is first poured in, and then the ore charged. The chemicals for generating the chlorine are charged in two portions, the first as soon as the ore is in, the second when the process is half finished; the time occupied is 4 to 8 hours, according to the nature of the ores. More chemicals must be used when copper is present. Sulphuric acid must be added in excess, so as to be sure that the chloride of lime is completely converted into sulphate. For 1 ton of

ore, if it contains no copper, the usual charge is 25 to 30 lbs. of chloride of lime and 30 lbs. of sulphuric acid at 66° B. At the Haile Mine, in South Carolina, the charge was only 17 lbs. of chloride of lime, and 20 lbs. of acid at 66° B. At the Phœnix Mine, where the ore is cupriferous, it was 40 lbs. of chloride of lime and 50 lbs. of sulphuric acid at 66° B. The water, ore and chemicals are charged through a manhole, the door of which is closed air tight by means of an indiarubber ring bearing against its flange. After this door is closed, the barrel is rotated at the rate of 12 revolutions per minute. As soon as free chlorine can be detected by the smell, the barrel is allowed to revolve for 1 hour longer, and the charge is then emptied on to a filter. A hole is provided in the barrel closed with a leaden valve, so as to enable the gases produced to be examined. Two charges are worked off in a day.

The charge falls out through the manhole, which is turned downwards, on to a filter placed beneath it. The latter consists in California of 3 divisions side by side, 18 inches high, rectangular in cross section; these divisions are of wood lined with sheet lead. The filter consists of a bottom layer of coarse quartz pebbles, a middle one of coarse sand, and an upper one of fine sand. From the filter the chloride of gold runs into a settling tank; the residue is then washed with water until the escaping filtrate carries no gold. The solution is allowed to stand 16 hours in the settling vats, which are 8 feet in diameter and 4 feet high, and is then run into the precipitating vessels. The yield by the Thies process is 92 per cent.

In the Black Hills the barrels are of cast iron, lined with lead, and hold from 5 to 10 tons; the larger ones have two charging doors; a filtering diaphragm is placed inside the barrel, which may consist of a grating or of a corrugated or perforated leaden plate, covered with a sheet of asbestos cloth; the gold solution is thus filtered off and the ore is leached inside the barrel. The filtered solution is run into settling tanks.

At Mount Morgan, the chlorinating barrels are made of eucalyptus wood, with iron heads, lead lined; their inside diameter is 3 feet 6 inches. The ores carry 4 to 5 ounces of gold to the ton, and the charge is one ton; 90 gallons of water, 40 to 48 lbs. of sulphuric acid at 66° B., and 35 lbs. of chloride of lime are added. The barrels make 6 revolutions per minute, and chlorination is complete in 2 hours. From the barrels the charge is transferred to vats with filters of the above kind, capable of holding 2½ to 3 tons of ore. The filtrate containing the chloride of gold is run into the precipitating vessels. As above mentioned, experiments are now being tried at

Mount Morgan on chlorinating in fixed oval iron vessels lined with lead. Each contains 2 stirrers, so set that the upper one pushes the ore towards the lower. Chlorine is generated outside the vessel, and is passed in continuously. Nothing is yet known as to the results attained.

Precipitation of Gold from the Solution of its Chloride

As already explained, the chloride of gold is dissolved in the chlorinating vessels themselves, when the ore is at rest during chlorination, and on filters either in these or in separate vessels when the ore is kept in motion during chlorination.

Sutton has proposed to separate the solution from the residues centrifugally. His machines, as erected experimentally at Mount Morgan, are furnished with a lining of asbestos cloth. The residues then remain in the central compartment, whilst the solution of gold chloride is thrown out; water or steam is admitted to wash the residues. Nothing is yet known of the efficiency of this method.

The solution of chloride of gold and the washings are often run into settling tanks before they pass to the precipitating tanks.

The gold is generally precipitated by ferrous sulphate or by charcoal. Recently also sulphuretted hydrogen has been used with good results, the remaining free chlorine being first converted into hydrochloric acid by means of sulphurous acid. Other precipitants such as sulphide of copper have been suggested, but have never come into regular use.

Ferrous sulphate is usually prepared at the works by dissolving iron in sulphuric acid.

When this salt is used, the precipitating vessels are wooden vats, painted like the chlorinating vats. They are wider at the bottom than at the top, their diameters being 5 feet 6 inches to 6 feet 6 inches at the top, and 6 feet 6 inches to 7 feet at the bottom, and their height 2 to 3 feet. The bottom is made of Portland cement or of a mixture of asphalt and cement heated together.

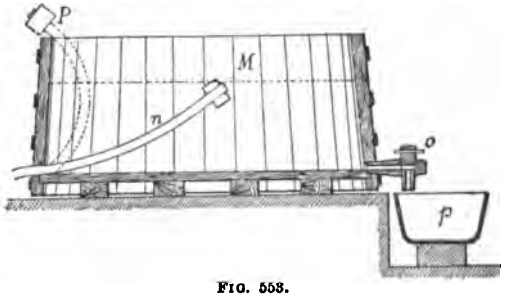


Fig. 553.

The construction of such a vat is shown in Fig. 553. After the gold has been precipitated and has been allowed to settle, the solution

is run off through the indiarubber hose *n*, the upper part of which is so fastened to a wooden float *M*, that the top end of the hose always remains in the fluid, and therefore falls as the level of the solution descends. In order to prevent any precipitated gold from escaping, the float *M* is made of such a size that the open end of the hose can never get down to the bottom of the vat. After the vat is cleaned out, any gold together with the solution still remaining in, it is run out through the tap *o*.

Whilst the ferrous sulphate solution is being added, the solution is stirred with wooden poles. The vat is then covered up, and the gold allowed to settle for at least 12 hours and sometimes 48 to 72 hours. At the end of this time, the supernatant solution is run off, as above described, into large settling vats, in which it deposits a certain amount of gold, and is then filtered through layers of sawdust or sand contained in wooden vessels, so as to collect the last particles of gold on these filters. The sawdust is burnt and the gold collected in the ashes; the sand is chloridised with the ores.

The precipitated gold is washed and treated with salt and sulphuric acid to remove the salts of iron still retained by it. In order to free it from water, it is wrapped in cloth and pressed, or filtered through paper; finally it is melted with salt, borax and nitre in graphite crucibles. The fineness of the gold thus obtained averages 800 to 960 per thousand, the impurities being usually iron and lead.

The precipitation with ferrous sulphate has the disadvantage that the precipitated gold only settles slowly from the solution, the latter still showing a purple colour, due to the presence of gold, for days after the precipitation. Solutions of gelatine and tannin, which accelerate the deposition of other precipitates, are inoperative in this case.

Sutton uses petroleum for the rapid collection of the precipitated gold and separates the latter from the solution centrifugally. Precipitation is performed in an iron vessel lined with lead, and provided with two stirrers. The solution of chloride of gold is stirred for only a few minutes with ferrous sulphate and petroleum, and solution and precipitate are then transferred together to small centrifugal separators. The residues remain in the central compartment, whilst the solution is flung out of it; the latter passes to a vessel in which the petroleum is separated from the iron solution and used over again to collect a fresh quantity of gold. Experiments on this method of precipitation are in progress at Mount Morgan, but nothing is known as to the results.

To obviate the above-mentioned disadvantage of slow deposi-

tion, charcoal was suggested by Davis as a precipitant for gold, and this method has been adopted in a number of works. The solution is allowed to run at the rate of 20 gallons per hour through a layer of charcoal powder 28 inches deep, supported by a quartz filter. To collect the last portions of the gold, the escaping solution is run through a second vat similarly arranged. According to Davis, 240 grains of charcoal are required to precipitate 19¼ grains of gold. In order to determine what proportions of gold were precipitated at different heights in the charcoal filter, 5,400 gallons of solution were allowed to run through a filter 20 inches deep; after precipitation of the gold, this was divided into 4 horizontal layers, each 5 inches deep, and the quantity of gold in each was determined. The results were as follows:—

Topmost layer	23·95	grains gold
Second „	2·99	„
Third „	1·22	„
Bottom „	1·62	„

At Mount Morgan the filtering vessels are conical in shape; the layer of charcoal is 2 feet deep, and each filter holds 9 to 14 bushels of charcoal.

The charcoal containing the gold is dried in the air and burnt in a muffle furnace; the ashes are treated with hydrochloric acid to remove soluble salts, washed, dried and melted in crucibles. At Mount Morgan, for instance, the ashes contain 75 per cent. of gold.

Both the methods of precipitation with ferrous sulphate and with charcoal, as hitherto practised, take much time. Sulphuretted hydrogen has recently been used at several works in order to precipitate and collect the gold more rapidly.

This method, for example, is being used with success at the Golden Reward Chlorination Works,[1] near Deadwood, South Dakota, U.S.A. It consists in first neutralising the free chlorine contained in the gold chloride solution by passing in sulphur dioxide, in accordance with the following equation:—

$$Cl_2 + SO_2 + 2H_2O = H_2SO_4 + 2HCl.$$

Sulphuretted hydrogen is then passed into the solution and the gold precipitated as auric sulphide, thus:—

$$2AuCl_3 + 3H_2S = Au_2S_3 + 6HCl.$$

The precipitation is rapid, and the precipitate is separated from the solution by means of a filter press.

[1] *Trans. Amer. I. M. E.*, 1892, p. 314. *Oesterr. Zeitschr.*, 1893, p. 148.

The sulphur dioxide is produced by burning sulphur, and is forced into the gold chloride solution by means of compressed air; the sulphuretted hydrogen is generated by the action of dilute sulphuric acid on sulphide of iron or coarse matte, and is forced in in the same way. The precipitate of sulphide of gold contains a certain amount of sulphur, together with sulphides of arsenic, antimony, copper and silver. It is roasted in a muffle furnace and melted in

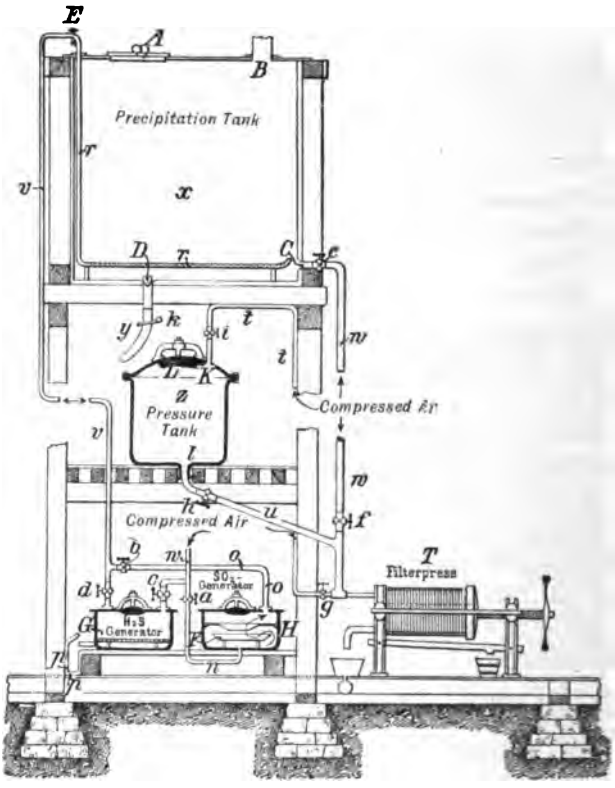


FIG. 554.

crucibles with nitre and borax. The gold so obtained has a fineness of 900 to 950 parts per thousand.

The arrangement of the precipitating plant is shown in Fig. 554. The precipitating tank, 10 ft. × 12 ft. and 12 ft. high, made of wood, lined with sheet lead, is shown at *x*. *A* is an opening, provided with a cover, through which the solution of chloride of gold (about 7,000 gallons) is run in, whilst at *B* is an outlet pipe for air and gases. The sulphur dioxide and sulphuretted hydrogen are admitted

through the lead pipe *r*, the lower horizontal portion of which is perforated by numerous holes, and which is coupled at *E* to the iron pipe *v*. The solution is run through the pipe *w* into the filter press *T*; *y* is a pipe that can be closed with a wooden plug, through which the precipitated sulphide of gold can be run out. *Z* is a pressure tank made of boiler plate, 4 ft. in diameter and 4 ft. 6 in. high, capable of standing a pressure of 150 lbs. to the square inch; it receives the precipitated sulphide of gold through the manhole *L* by means of the indiarubber hose pipe *y*. Compressed air is forced in through the pipe *t*, and the precipitate is thus forced into the filter press *T* through the pipe *u*.

H is the sulphur dioxide generator, which is also made of boiler plate and capable of standing a pressure of 150 lbs. per square inch. It is 2 ft. 3 in. high and 4 ft. in diameter. Sulphur is burnt in it by means of compressed air. The sulphur is contained in the cast iron pan *F*, whilst compressed air is admitted by the pipe *n*. The sulphur dioxide, together with the excess of air, pass through the pipe *o*, when the valve *b* is opened, into the tubes *v* and *r*, and thence into the solution of chloride of gold.

The sulphuretted hydrogen is produced in the generator *G*, of the same make and dimensions as the former, but lead lined as a protection against the action of the sulphuric acid. Two inches above the bottom is a perforated false bottom made of sheet lead; this carries the sulphide of iron, which, together with the sulphuric acid, is charged through a manhole. The valve *d* being open and *b* closed, the sulphuretted hydrogen passes through the pipes *v* and *r* into the precipitating tank. By drawing out a plug at the side, the liquid in the generator is run out into the asphalted wooden discharge trough *p*. To promote the evolution of sulphuretted hydrogen, compressed air is forced into the generator through the pipe *n*, the valve *c* being opened and *a* closed. The air escapes, charged with sulphuretted hydrogen, into the solution of chloride of gold.

The neutralisation of the free chlorine and the precipitation of the gold take place rapidly. After the precipitation, the precipitate is allowed to settle for 2 hours, and the supernatant solution is drawn off through the pipe *w* into the filter press, by means of its own hydrostatic pressure, the precipitating tank being placed 25 feet above the press. In 3 to 4 hours after precipitation, the tank is ready to receive a fresh charge of gold chloride solution. The precipitated sulphide of gold collects on the bottom of the precipitation tank; every two months it is run into the pressure tank and thence forced into the press.

Freshly precipitated sulphide of copper has also been proposed as

a precipitant for the gold; this substance is to be contained in a series of filters placed one below the other, through which the gold solution would have to percolate. Sulphide of copper (Cu S) precipitates gold with the formation of sulphate of copper, from which latter salt sulphide of copper is to be regenerated by means of sulphuretted hydrogen, and to be again used as a precipitant.

The general arrangement of a certain number of works, notable as being well laid out, is shown in Figs. 555 to 559.

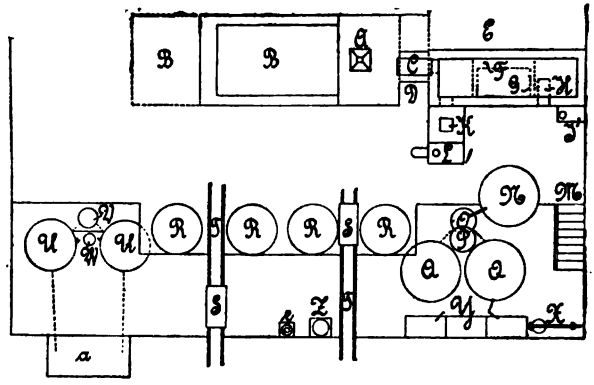


FIG. 555.

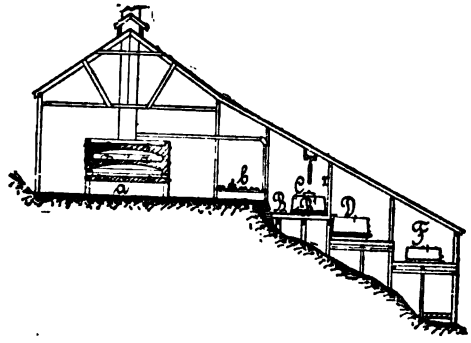


FIG. 556.

Fig. 555 is the ground plan of a works designed by Aaron to treat argentiferous gold ores. On the one side is the plant for the dry, on the other for the wet processes. The calcining furnace is shown at *B*, with its charging hopper *A*; *F* and *G* are arrangements for drying the ore. There is a furnace at *L* for melting the gold, and the stack is shown at *K*. *R* are the chlorination vats; after the gold has been leached out in these, the silver is leached out by means of hyposulphites. The gold precipitating vats are shown at *U*, those for silver at *Q*; *N*

is a tank for holding hyposulphite solution, and *Z* the chlorine generator.

Figs. 556 and 557 show the works at Providence Mine in Nevada City, California; here the plant is arranged in terraces. The calcin-

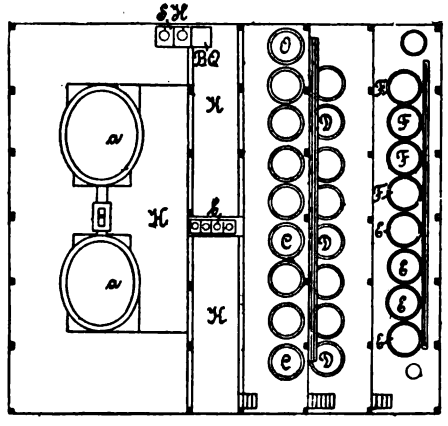


FIG. 557.

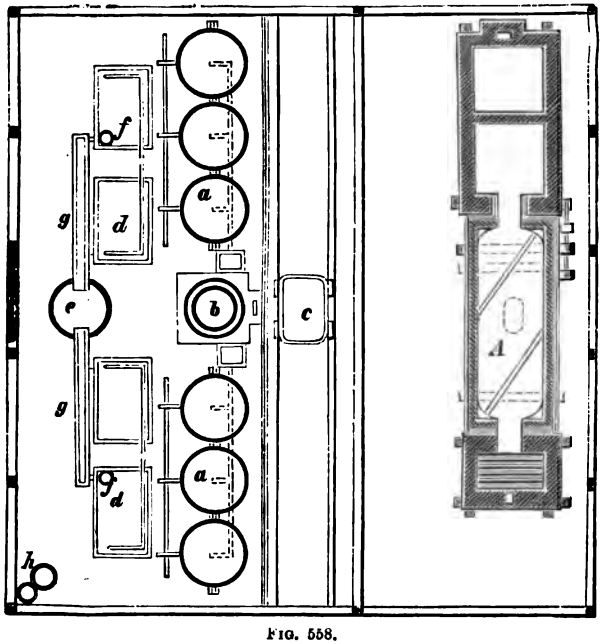


FIG. 558.

ing furnaces with oval hearths are shown at *a*; *b* are the chlorine generators standing on the same level; *C* are chlorinating vats, the covers of which can be lifted by a travelling set of pulley blocks; *O* is

a vat for hyposulphite solution; *D* the vats in which the chloride of silver is dissolved out by means of it; *E* are gold precipitating vats, and *F* vats for throwing down the silver.

Figs. 558 and 559 represent a plant for treating gold ores that do not carry silver. *A* is a Brückner calciner; *a* are chlorinating vessels carried on trunnions; *b* is the chlorine generator; *d* are the precipitating vats; *e* is a vat filled with sawdust, through which the liquor

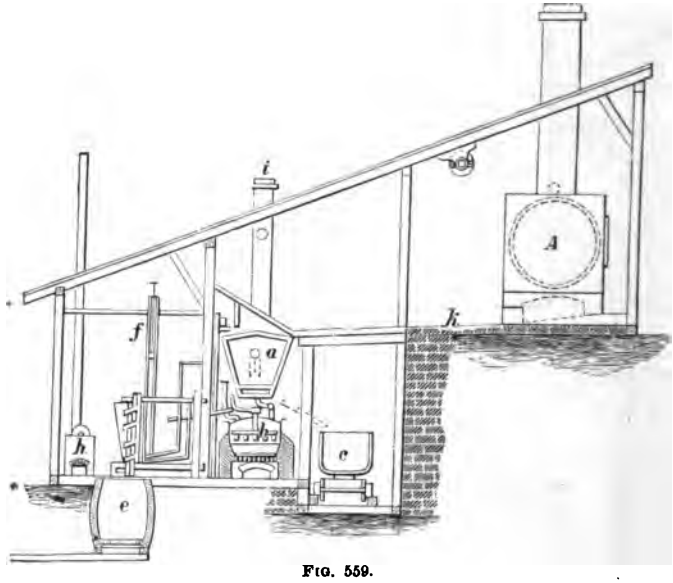


FIG. 559.

from the precipitating vats is filtered. The exhausted residues are dumped out of the chlorinating vessels *a* into the car *c*.

With the Plattner process, the extraction of gold is between 90 and 94 per cent., according to the nature of the ores. By leaching out the chloride of silver with hyposulphites, the extraction of silver is at least 60 per cent.

Of other methods for chlorinating gold that have not come into use, that of Patera may be mentioned, who employs a cold solution of common salt saturated with chlorine, as also that of Rössner, who submits the ores to a chloridising roasting, extracts the silver by means of a hot solution of salt, and finally the gold with a cold solution of salt containing chlorine. Kiss's proposal has already been referred to. Attempts have also been made to extract the gold from ores by means of aqua regia, but had to be given up on account of the high price of the solvent.

Extraction of Gold by Means of Bromine

This method was proposed by Wagner, Föhr, and others, but has not received any extended application on account of the high price of this solvent. Wagner [1] has treated calcined iron and arsenical pyrites with bromine water, filtered off the solution, and passed sulphur dioxide into the filtrate. By this means the ferric bromide contained in the solution was reduced to ferrous bromide, which latter substance precipitated the gold on boiling, after the excess of sulphur dioxide had been got rid of.

The bromine method has been used at Rapid City, Dakota, where barrels similar to those used in chlorination are employed. After ore and water are charged into the barrel, bromine, in the proportion of 2 to 4 lbs. to the ton of roasted ore, is poured in, and is allowed to act for half an hour to an hour and a half, according to the nature of the ores, the barrel being revolved all the time. The bromide of gold is then dissolved out and filtered in a separate leaching vessel, and the gold precipitated by means of sulphuretted hydrogen.

In an experimental works at Denver, Colorado, managed by E. C. Engelhardt, bromine is used in a hydrochloric acid solution, which acts much more energetically than does an aqueous one, revolving barrels being employed.

According to a method recently suggested by C. Lossen, which is to be applied at a works in Oregon, the ore, raw or calcined, is mixed in a revolving barrel with an alkaline solution of bromine, which is allowed to act until all the gold is dissolved. When the mixture is no longer alkaline, a fresh quantity of bromine solution is added, and it is then filtered. The gold thus passes into solution as an aurate, whilst the iron and other metals remain behind as hydrates, and the bromine is dissolved as bromide of potassium. The filtrate is passed through vessels containing a mixture of pieces of iron and charcoal or coke, by which the gold is completely precipitated; the resulting liquor, containing chiefly bromide of potassium, is run through long troughs, where it is decomposed by an electric current. This produces an alkaline solution of hypobromite, which cannot of course contain free bromine, but which has the property of dissolving fine gold, and can accordingly be used as a solvent for leaching fresh quantities of ore.

Treatment of Telluride Gold Ores

These ores are now being treated at Schemnitz with hot concentrated sulphuric acid, and the mixture dropped into water

[1] *Dingler's Journal*, 218, 253.

containing hydrochloric acid. The tellurium is thus obtained in solution and is precipitated by means of zinc. The gold remains in the residues, which are smelted with lead ores.

The MacArthur-Forrest Process[1]

This process, the so-called cyanide process, depends upon the solution of the gold as auro-potassic cyanide ($KAuCy_2$) by means of a dilute solution of potassic cyanide, and the precipitation of the gold by means of zinc. It was proposed in 1890 by MacArthur and Forrest, and introduced into a number of works in the Transvaal, South Africa, and has also been employed in New Zealand, Queensland, and other Australian colonies, Mexico, the United States, India, &c.

Although the process is apparently simple, the readiness with which cyanide of potassium is decomposed and the difficulties in the way of regenerating it from the zinc-bearing solutions after the gold has been precipitated, are obstacles that have prevented its employment in a number of cases.

As far as experience has gone hitherto, it is best adapted for *free milling* ores, that is to say such ores as readily give up their gold contents to mercury. But if these ores carry coarse gold, or are rich, the process cannot be employed to advantage, because coarse gold is but slowly attacked by the cyanide solution, whilst rich ores would retain too much gold in the residues.

Many pyritic ores are, however, also adapted for this process, though in many cases the cost of treatment is greater than by the Plattner process.

Whether, and to what extent, it may be possible to overcome the obstacles that have prevented the adoption of this process at many works, cannot be stated decisively at the present time.

The process has been employed most successfully in the Transvaal. The ores there are said to average about 9 dwt. of gold to the short ton of 2,000 lbs. They are stamped and amalgamated by means of inside amalgamation and copper tables; the pyrites in the pulp is concentrated generally by means of Frue vanners, and chlorinated. The resulting tailings, which are said still to contain on the average

[1] MacArthur, *Journal Soc. Chem. Ind.*, March 31, 1890. *Memorandum on the Treatment of Refractory Ores by the MacArthur-Forrest process*, Adelaide, Frearson and Bros., 1891. Janin, *The Mineral Industry*, 1892. Butters and Clennell, *Eng. and Min. Journ.* 1892, pp. 341, 365, 392, 416. Molloy, New Cyanide process *Eng. and Min. Journ.* 1892, p. 155. Dr. A. Scheidel, *The Cyanide process*, Sacramento, 1894. Butters and Smart, Plant for the Cyanide process, *Trans. Inst. C. E.*, 1895, Pt. iii.

3½ dwts. of gold to the ton, form the material chiefly treated by the MacArthur-Forrest process, which extracts the gold, leaving only 1 dwt. 4 grs. to the ton behind. It must be noted that not the whole of the tailings can be treated, but only the coarser portions, which is allowed to settle in large reservoirs, the finer portions, known as *slimes* which amount to rather over one-third of the tailings, offering too great an obstacle to the passage of solution through them. In some cases the pyrites are not separated from the tailings, but are subjected together with them to the cyanide process.

The process may be divided into:—1. Solution of the gold. 2. Precipitation of the gold. 3. Treatment of the precipitated gold.

I. Solution of the Gold

Bagration[1] first announced the solubility of gold in potassium cyanide in 1843, and Faraday also proved this fact.

Various views have been put forward as to the chemical changes that take place when the gold is dissolved. According to Elsner,[2] gold will only dissolve in cyanide of potassium in the presence of oxygen, according to the reaction:

$$Au_2 + 4KCy + O + H_2O = 2KAuCy_2 + 2KHO.$$

Rœssler also enumerated gold and silver in 1866[3] amongst the metals which require the oxygen of the air in order to dissolve in cyanide of potassium, whereas palladium, zinc, iron and copper can abstract oxygen from the water of the aqueous solution of potassium cyanide, and evolve hydrogen on dissolving.

According to MacArthur and Janin,[4] oxygen is not necessary for the solution of gold, which takes place in accordance with the following equation:

$$Au + 2KCy + H_2O = KAuCy_2 + KHO + H.$$

As, however, very small quantities of oxygen are required, namely, 15·96 parts of oxygen for 396·6 parts of gold, or 1 part of oxygen for approximately 25 parts of gold, it may be assumed that in the absence of air sufficient oxygen would be contained in the powdered ore and in the solution to assist in dissolving the gold as above. There is, therefore, no reason at all for denying the action of oxygen.

[1] *Journ. f. Prakt. Chem.*, xxxi. 367.
[2] *Ibid.*, xxxvii., 333.
[3] *Inaugural Dissertation*, Göttingen, 1866.
[4] *The Mineral Industry*, 1892.

This question has practically been set at rest by the very searching investigation of Maclaurin,[1] who has confirmed the correctness of Elsner's reaction by careful quantitative experiments.

Moldenhauer has based a process upon the part played by oxygen in the solution of gold, which has given very good results in the experiments hitherto tried with it. He (for the Frankfort-on-the-Maine Parting Works) uses an aqueous solution of ferricyanide of potassium and potassic cyanide, which acts as follows :—

$$2K_3Fe_2Cy_6 + 4KCy + Au_2 = 2AuKCy_2 + 2K_4FeCy_6.$$

At the experimental station of the above company at Battigio, on Monte Rosa, this solution was found to extract some 10 dwt. 11 grs. per ton of gold from arsenical pyrites containing 13 dwt. 2 grs. per ton.

Messrs. Sulman and Teed have proceeded upon somewhat similar lines in the process patented by them ; this depends upon the employment of a haloid compound of cyanogen, together with cyanide of potassium as a solvent. Preference is given to the bromide of cyanogen, which is stated to be easily prepared and convenient for practical use. With chloride of cyanogen the reaction is stated to be :—

$$CyCl + 3KCy + Au_2 = 2KAuCy_2 + KCl.$$

The process does not yet seem to have come into practical use, but is being tried on a working scale at the Day Dawn Mine, Western Australia, where the first trial on a 300 ton parcel of tailings assaying 4 dwt. 7 grs. to the ton showed that only 12 grs. to the ton escaped extraction.[2]

According to theory the quantity of cyanide of potassium required for the MacArthur-Forrest process should be 130·04 parts by weight for 196·8 parts of gold, so that 2 parts of cyanide should suffice for 3 parts of gold. Actually, however, with ores of low and medium gold contents, some 40 parts of potassium cyanide are consumed to one of gold. The cause of this enormous consumption lies in the readiness with which potassic cyanide is decomposed, and in the decomposing action which the constituents of many ores exert upon it.

Thus cyanide of potassium is decomposed by the carbon dioxide and the oxygen of the air, as also by caustic alkalies, by sulphuric acid, and by sulphates of iron.

[1] *Journ. Chem. Soc.*, 1893, lxiii., p. 724.

[2] Western Australia, *Report of the Department of Mines for* 1895, p. 36.

Carbon dioxide and oxygen act respectively as follows :—

$$2KCy + CO_2 + H_2O = 2HCy + K_2CO_3.$$
$$KCN + O = KCNO.$$
$$2KCNO + 3O = K_2CO_3 + CO_2 + N_2.$$

Free alkalies, which are generally contained in commercial potassium cyanide, and which are added to neutralise acids and to decompose the iron salts contained in the ores, bring about a decomposition, mainly due to water, whilst the alkalies themselves remain unchanged. This decomposition takes place especially when gold is precipitated by zinc, and is as follows according to Butters and Clennell :[1]—

$$KCN + 2H_2O = NH_3 + KHCO_2.$$
$$H_2O + KCy = HCy + KHO.$$

Pyritic gold ores that have been exposed for any considerable period to atmospheric action, contain sulphates of iron and free sulphuric acid, as decomposition products of the iron pyrites.

Ferrous sulphate forms with potassic cyanide, first, ferrocyanide of potassium, and then Prussian blue in accordance with the following equations :—

$$FeSO_4 + 2KCy = FeCy_2 + K_2SO_4.$$
$$FeCy_2 + 4KCy = K_4FeCy_6.$$
$$3K_4FeCy_6 + 6FeSO_4 + 3O = Fe_2O_3 + 6K_2SO_4 + Fe_7Cy_{18}.$$

Ferric sulphate produces with potassic cyanide, hydrocyanic acid, sulphate of potash and ferric hydrate, thus :—

$$Fe_2(SO_4)_3 + 6KCy = Fe_2Cy_6 + 3K_2SO_4.$$
$$Fe_2Cy_6 + 3H_2O = Fe_2(OH)_6 + 6HCy.$$

A mixture of ferrous and ferric sulphates produces with potassic cyanide either Prussian or Turnbull's blue, according as the former or the latter salt predominates, thus :—

$$18KCy + 3FeSO_4 + 2Fe_2(SO_4)_3 = 9K_2SO_4 + Fe_4(FeCy_6)_3.$$
$$12KCy + 3FeSO_4 + Fe_2(SO_4)_3 = 6K_2SO_4 + Fe_3(FeCy_6)_2.$$

Free sulphuric acid converts potassic cyanide into the sulphate with the evolution of hydrocyanic acid.

Silver and base metals (zinc and copper) are also dissolved by potassic cyanide. MacArthur and Forrest maintain that dilute solutions of potassic cyanide (0·2 to 0·8 per cent. of KCy) only dissolve gold and silver, whilst attacking but slightly any base metal

[1] *Eng. and Min. Journ.*, 1892, p. 392.

that may also be present. According to Butters and Clennell,[1] however, base metals are attacked to such an extent that ores containing them in considerable quantity are not suited to this process, as has indeed been shown by experiments in California and Australia. Sulphide of silver[2] is not attacked, but metallic silver is dissolved by potassic cyanide, as shown in the following equation:—

$$Ag_2 + 4KCy + O + H_2O = 2KAgCy_2 + 2KHO.$$

Sulphide of copper is dissolved as a sub-sulpho-cyanate.[3]

The loss of cyanide may be controlled by using pure cyanide and pure water, by suitably preparing the ores beforehand, and by excluding air during the process of solution.

The ore to be treated is crushed by rolls or stamps to pass a sieve of 40 to 60 meshes to the linear inch. Tailings from the stamp-mills, such as are treated in South Africa and other places, are in a suitable state of division for the process. Certain surface ores in the Transvaal have been treated successfully when crushed quite coarsely. Wet ore is dried before being leached.

Cyanidation is performed in tanks with the ore at rest; the treatment with agitation of the ore (in barrels) necessitates the consumption of a good deal of power, and causes more rapid decomposition of the cyanide. Most works have therefore abandoned this method.

Circular vats are mostly employed at present. They are generally constructed of deal staves[4] 4½ inches to 9 inches wide by 3 inches thick, held together by hoops of round iron 1 inch to 1⅛ inch in diameter with screwed ends to allow of their being drawn up tight. Some vats are fitted with doors secured like man-hole doors in the bottom or the sides, for discharging the exhausted tailings. The bottom is made of 9 inch by 3 inch deal planks checked into the staves. The false bottom consists of a filter of cocoanut matting, sometimes protected by a top filter of jute cloth; it rests upon a frame of wooden slats 3 inches deep and about 1 inch wide; the space between the true bottom and the filter is sometimes filled with a layer of pebbles and coarse sand. The solution is drawn off through an iron pipe in the bottom of the vat; all pipes and cocks are of iron, and direct acting steam pumps and centrifugal pumps have both been used. Exceptionally square brick vats and circular pits in solid ground lined with cement have been employed, but wooden vats are preferred.

[1] W. Bettel, *Eng. and Min. Journ.*, 1892, p. 416.
[2] *Ibid.* [3] *Ibid.*
[4] Butters and Smart, *Trans. Inst. C. E.*

The capacity of the first tanks erected in South Africa, which were square and about 3 feet 6 inches deep, was 35 to 50 tons. Those now used at the Robinson Works, 20 feet in diameter and 8 feet deep, hold 75 tons, those at Langlaagte Estate, 40 feet in diameter and 14 feet deep, 400 tons, and those at the New Primrose Mine 600 tons.

For the reasons above given, when ores contain free sulphuric acid and sulphate of iron, these substances must first be removed before cyanidation. For this purpose they are first treated with water in the leaching tanks to remove free sulphuric acid and neutral iron salts. To neutralise the basic salts they are next leached with caustic soda solution or lime water, which convert the ferric sulphate into hydrate, thus:—

$$Fe_2O_3SO_3 + 2NaHO + 2H_2O = Fe_2(HO)_6 + Na_2SO_4.$$
$$Fe_2O_3, 2SO_3 + 4NaHO + H_2O = Fe_2(HO)_6 + 2Na_2SO_4.$$

Lime is preferable to caustic soda because it does not decompose the potassic cyanide so readily, and has less action on the zinc in the precipitating tanks.

Freshly precipitated ferrous hydrate is able to convert potassium cyanide into ferrocyanide:—

$$Fe(OH)_2 + 6KCy = K_4FeCy_6 + 2KHO.$$

This reaction also causes losses of cyanide. Brown hæmatite does not affect cyanide of potassium.

Leaching is performed first with strong, then with weak cyanide solution. The former contains 0·6 to 0·8 per cent. potassic cyanide; it is allowed to act for 12 hours, is then run off, and another solution of equal strength run on. This is allowed to remain for 6 to 12 hours, according to the richness of the ore. For each ton of ore, about ½ ton of cyanide solution of the above strength is required. The weak solution, which is run on after the strong solution has been run off, contains 0·2 to 0·4 per cent. of potassium cyanide. The solution used for this purpose is the spent liquor after the gold has been precipitated by zinc, and which can be used as long as it does not contain too much zinc salt and still carries sufficient free cyanide, being always made up to the strength required. It is allowed to act for 8 to 10 hours on the ore; about ½ ton of this solution is required to the ton of ore. The consumption of cyanide is less on ores consisting only of quartz and brown hæmatite; thus at the Robinson Mines 20 tons of solution sufficed to extract 75 ozs. of gold from 40 tons of ore.

The leaching is followed by washing with water, and then the residues are emptied out of the vats. This is done in various ways. They may be simply shovelled out of small vats; from larger ones they are sometimes emptied through side or bottom doors into trucks running on rails below the vats. Sometimes the vats are fitted with large doors, which can be drawn up, and trucks run into the vats themselves; or the tailings may be hoisted out by cranes. Where water power is abundant and the grade of the ground suitable, they may be sluiced out and washed away.

With suitable ores, the process has been so arranged that the same solution circulates successively through several vats filled with ore. A solution richer in gold is thus obtained than in the other method of cyanidation, and as less solution comes in contact with the zinc during the precipitation, less cyanide is wasted; at the same time the precipitated gold is also purer.

The solution of cyanide used for leaching is prepared in most works by dissolving commercial potassium cyanide (containing 72 to 78 per cent. of pure potassic cyanide) in the least possible quantity of water, and by diluting this concentrated solution with wash water or with spent liquor to the required degree. At some works (*e.g.*, Robinson Mine) potassium cyanide in lumps is added during the leaching in such quantity as to keep the solution at its original strength.

II. Precipitation of the Gold

The best precipitant so far tried, has been found to be zinc in the form of bright turnings. The precipitation of the gold occurs in accordance with the following equation:—

$$2KAuCy_2 + Zn = K_2ZnCy_2 + Au_2.$$

According to this, 65·1 parts of zinc should precipitate 393·6 parts of gold, or 1 part of zinc to 6 parts of gold. Actually in working on a large scale, 453 parts of zinc will only precipitate 32 parts of gold. The cause of this enormous zinc consumption lies in a number of subordinate reactions that take place during precipitation. According to Butters and Clennell,[1] the contact of the zinc with the precipitated gold produces an electrical current which decomposes water, zinc being oxidised by the oxygen generated, and zinc hydrate being produced according to the following reaction:—

$$Zn + 2H_2O = H_2 + Zn(OH)_2.$$

[1] *Eng. and Min. Journ.*, 1892, p. 416.

The hydrate of zinc is dissolved by potassic cyanide with the formation of caustic potash, thus :—

$$Zn(OH)_2 + 4KCy = K_2ZnCy_4 + 2KOH.$$

The caustic alkalies contained in the solution convert a part of the zinc into potassio-zincic oxide with the evolution of hydrogen; this compound precipitates zinc cyanide as a white precipitate from the potassio-zincic cyanide. With caustic soda the reactions are as follows :—

$$Zn + 2NaOH = Zn(ONa)_2 + H_2.$$
$$2H_2O + Zn(ONa)_2 + K_2ZnCy_4 = 2ZnCy_2 + 2NaOH + 2KOH.$$

These reactions limit the accumulation of zinc in the solutions.

Potassio-zincic cyanide is incapable of dissolving gold. As all attempts to regenerate potassium cyanide from this compound have hitherto failed, the potassic cyanide contained in it is lost, as far as gold extraction is concerned.

The zinc turnings are prepared by turning a number of discs of zinc, fastened together so as to form a cylinder, in a lathe with an ordinary chisel; these turnings are prepared immediately before being used to prevent any oxidation of their surface. Granulated and sheet zinc do not present sufficient surface, whilst zinc dust and zinc amalgam possess the necessary surface, but choke up as soon as the current of solution through them is interrupted. Sulman and Teed have suggested the use of zinc fume.

The precipitation boxes or zinc boxes are made of wood as a general rule, though steel boxes have been used in California. The boxes are set on an incline, and are divided by transverse partitions so as to form a number of alternately wide and narrow compartments, through which the solution flows alternately upwards and downwards. In each of the wider divisions, in which the solution flows upwards, is set a deep sieve with its bottom made of wire sieving, with 4 holes to the linear inch. These sieves rest on cleats and can be lifted out. The zinc turnings are charged into them; the gold solution flowing upwards deposits the gold underneath the shavings, whence it can fall through the sieve on to the bottom of the precipitating box. Zinc boxes are 18 to 40 feet in length, about 1 foot 6 inches to 3 feet wide, and 2 feet to 2 feet 6 inches deep. Butters and Smart (*loc. cit.*) give as a rule that for each ton of solution to be precipitated per hour, 21 cubic feet should be allowed in the zinc box, and as the average rate of flow of the solution 26 feet per hour.

A cubic foot of zinc shavings[1] weighs from 3 to 6 lbs., and it exposes about 40 square feet of surface to the pound weight.

At the Robinson Works the zinc boxes are 20 feet long and 2 feet square in cross section; they are divided into 10 compartments, 1 foot 9 inches long. The first is left empty as a settling box; the next 7 are charged each with 1½ cubic feet of shavings, weighing altogether 40 lbs.; the last two divisions serve to catch particles of gold that might otherwise be carried off by the solution. The strong and weak solutions are passed through separate zinc boxes, and, after the gold has been precipitated, are run into separate storage tanks, whence they are pumped back into the solution vats.

The zinc boxes lie at a lower level than the leaching vats. The gold-bearing solution is allowed to run slowly through the zinc shavings, which precipitate the gold as a black slime. Besides gold, silver and any base metals in the solution that are more electro-negative than zinc are precipitated by it. The proportion of cyanide in the escaping liquor is far less than in the entering solution, on account of the reactions above described. However rich in gold the entering solution may be, it should only contain a few grains to the ton at the outflow.

Gold is precipitated most rapidly in the first divisions of the zinc boxes; the zinc in these is consumed with proportionate rapidity, and is then replaced by shavings from the following divisions, all being moved up and fresh zinc shavings added in the last compartments.

The precipitated gold is cleaned up once or twice a month. Any gold adhering to the shavings is rubbed off as far as possible, and then the sieves with the undissolved zinc turnings lifted out. The gold that remains is either allowed to settle in the zinc boxes, the solution above it drawn or syphoned off and the slimes scraped out, or else gold and solution are drawn off together through plug-holes, and the gold allowed to settle outside the zinc box. The residual slimy mass is rubbed with sticks tipped with indiarubber on a sieve of 40 holes to the linear inch; pieces of zinc are thus left on the sieve, and these are returned on top of the zinc shavings in the first divisions of the zinc box. The gold and a part of the zinc in a state of fine division, are forced through the sieve, together with the remaining solution.

This slime is drained as far as possible, and is ready for further treatment; it consists of finely divided gold and silver, considerable quantities of zinc, also lead, tin, copper, antimony, arsenic, mercury

[1] Scheidel, *op. cit.* p. 53.

according to Scheidel, organic matters and other impurities from the zinc and the ores.

The composition of slimes at the Mercur mines, Utah,[1] is:—

Zn	39·1
$CaCO_3$	36·7
Au	4·4
Cy	3·5
S	2·6
Fe	2·4
Residue	6·0
	94·7

III. Treatment of the Precipitated Gold

The gold precipitate is dried, and may be simply melted with sand, borax and carbonate of potash. A crucible filled with the fused mass contains 100 to 150 ounces of gold alloy. The zinc volatilises to a considerable extent on melting, and carries off notable quantities of gold. Dust chambers to collect the flue dust are used at some mines.

The slags produced in smelting, which are rich in zinc, also carry gold and must be retreated separately—best by smelting with lead ores. The bar gold thus obtained is 650 to 800 fine, and contains silver, lead, zinc, and often small quantities of copper. In South Africa, where the slimes average about 33 per cent. of gold, they are generally heated in trays with nitre before fusion with the above fluxes.

Another method that is much used consists in calcining the gold slime in a small flat-bedded reverberatory furnace, by which means most of the zinc is oxidised before fusion.

Treatment with acid is not unusual in South Africa; it is preferred by Scheidel,[2] who treats the gold slime at the Utica Mine, California, in tubs with dilute sulphuric acid. The bullion is then allowed to settle, the liquid syphoned off, and the bullion slimes washed till all soluble salts are removed. The slimes are then dried in a small muffle furnace, and fused with borax and carbonate of soda in a graphite crucible. The resulting bullion is 946 fine.

Bisulphate of soda and fluor spar have also been used as fluxes in melting.

[1] *Eng. and Min. Journ.*, 1891, p. 440. [2] *Op. cit.* p. 93.

Other Methods of Precipitation

The employment of zinc as a precipitant is open to a number of objections; cyanide of potassium cannot be regenerated from the potassio-zincic cyanide, so that it becomes necessary to discharge this substance from time to time, a very objectionable proceeding on account of its poisonous properties; zinc when used as a precipitant causes considerable loss of potassic cyanide; the consumption of zinc is very heavy, and it can only be used in the form of bright turnings, which have to be prepared at the works themselves directly before use; the zinc-bearing gold slimes are difficult of treatment, and this always entails considerable loss of gold.

It is therefore natural that attempts have been made to replace zinc by other precipitants, but so far without success. The usual precipitants for gold, like ferrous sulphate, oxalic acid, sulphuretted hydrogen and sulphide of sodium, cannot be employed. Molloy has proposed an amalgam of potassium or sodium, and the Gold and Silver Parting Works of Frankfort-on-the-Maine recommend aluminium. Potassium or sodium amalgam precipitates gold from the auro-potassic cyanide solution, with the formation of gold amalgam and regeneration of potassic or sodic cyanide, the latter being as effective as the former as a solvent for gold. Hitherto it has not been possible to prepare these alloys cheaply enough.

Molloy prepares the sodium by the electrolysis of sodic carbonate.[1] He allows the gold solution to flow through a shallow vessel, the bottom of which is covered by a layer of mercury. In this vessel there is a cylindrical vessel without bottom, so placed that its lower edge dips below the surface of the mercury. The latter vessel is filled with sodic carbonate and contains a leaden rod, which forms one of the poles of an electric circuit, the quicksilver forming the other. When the circuit is closed the sodic carbonate is decomposed, the sodium being separated at the mercury pole and alloying with it. The sodium of the sodium amalgam thus formed precipitates the gold from its solution and replaces it; the gold is taken up by the mercury and amalgamated by it.

With respect to the use of aluminium, Dr. Roessler finds that sheet aluminium has the advantage of precipitating gold from feebly alkaline solutions at a comparatively rapid rate, regenerating the cyanide of potassium at the same time, as shown by the following equation:

$$6(AuKCy_2) + 6KHO + Al_2 = 6Au + 12KCy + Al_2O_3 + 3H_2O.$$

[1] *Eng. and Min. Journ.*, 1892, pp. 155, 365.

Should either of these methods prove applicable in practice, a great step will have been made in the cyanide process.

Electrolytic precipitation has been introduced by Messrs. Siemens and Halske, was first used at the Worcester Gold Mining Company's Works in the Transvaal, and is now being used successfully at several others. The solution is passed through a tank about 7 feet wide and 3 feet deep, containing a series of anodes of plate iron and of cathodes of thin sheet lead, a current density of about 0·06 ampère per square foot of surface being used. With cathodes 1½ inches apart, a current strength of 4 volts is sufficient, and 5 I.H.P. will work a plant treating 3,000 tons per month. When the current passes, the gold is precipitated on the lead cathodes; a certain amount of Prussian blue is at the same time formed at the anodes, which is retained in the canvas bags that cover the latter. The lead foil cathodes, with a film of gold adhering to them, are removed when they have to be cleaned up, replaced by fresh sheets, and smelted into bars, the base lead bullion thus formed, which contains 2 to 12 per cent. of gold, being cupelled; the result is very pure gold bullion alloyed only with a certain amount of silver. The lead consumption is about 750 lbs. per month, and iron 1,080 lbs. in a plant treating 3,000 tons. When this method is adopted, it is found practicable to leach the ores with much weaker solutions than are otherwise employed, the strong solution containing 0·05 to 0·08 per cent. of potassic cyanide, and the weak 0·01 per cent. By this means a considerable saving in the cyanide consumption is effected, and the process seems to be well spoken of in many respects. Its cost is said to be about equal to that of zinc precipitation.

Direct Cyanidation

A method has recently been introduced at the George and May Mines, and is being tried in West Australia and in Queensland, for treating ores direct with cyanide. It is only applicable to porous ores where the gold is free but very fine.

At the George and May Mines the ore is crushed in a Gates crusher to about ¼ inch mesh. This is then charged without any screening into the cyaniding vats and treated with four washes of cyanide solution of the following strengths:

1st wash	0·06	per cent.	of potassium	cyanide.
2nd „	0·28	„	„	„
3rd „	0·10	„	„	„
4th „	0·05	„	„	„

The ore carries about 5 dwts. to 5¼ dwts. of gold, and yields about

4 dwts. to the ton by this treatment, so that an extraction of about 75 per cent. is obtained. The ore is a surface ore, very friable and porous, and completely oxidised. The applicability of the method to ores of more usual character has not yet been proved.

General Remarks

Although cyanide of potassium taken internally is one of the deadliest poisons, the number of accidents in carrying out the cyanide process appears to be very small. The men engaged in clearing up the precipitating boxes and in smelting the precipitate complain of headache, giddiness, and lassitude, and suffer from sores that generally break out on the arms.

The MacArthur-Forrest process has been used successfully in the gold mining districts of the Transvaal, especially on ores from the upper levels of the gold deposits, which contain gold in a state of extremely fine division, and consist chiefly of quartz and brown iron ore; also upon the tailings of these ores after they have been amalgamated, and either with or without previous removal of the sulphides by concentration; opinions are greatly divided on the utility of this operation. The extraction averages 70 to 80 per cent. As already pointed out, only the coarser portions of the tailings are in a condition suitable for treatment by cyanidation; the very finely divided portion or *slimes* has to be separated out first, and hitherto no process has been devised for successfully treating the slimes. One of the points at present under discussion is whether the cyanidation vats should be filled direct from the batteries, spitzkasten or spitzlutten being used to separate out the slimes, or whether the sands should first be run into a settling tank and filled by hand into the cyaniding vats. In the latter case the sands do not pack so tight, and percolation is more readily effected. This method has a good many advocates; where it is used, the system of filling the settling tank by means of Butter's and Mein's distributor seems to have been largely adopted.

In Australia, at the Ravenswood works in Queensland, an extraction of 84 to 89 per cent. was obtained on ores with 7 to 12 ounces of gold to the ton. Similar results were obtained at the Freehold United Mine, near Daylesford, in Victoria.

In New Zealand, at the Karangahake Works near Auckland, 80 to 91 per cent. of gold and 28 to 83 per cent. of silver were extracted from various kinds of ores.

The process is also being used in the United States, notably at the

Mercur Mines in Utah, the Utica Mine in California, Cripple Creek district in Colorado, and a few other localities.

Results obtained experimentally are as a rule markedly more favourable than those obtained on a large scale, because in the former case relatively small amounts of ores or tailings are treated with relatively large quantities of cyanide solutions of equal strength.

As the cyanide method is yet in its infancy, and its improvement and perfection open a wide field for metallurgical research, it remains still to be seen how it will develop and to what extent it can be used with advantage on the various kinds of gold ore. The first points to determine are how the solution of gold in a solvent containing ferricyanide of potassium as well as cyanide compares with the use of pure cyanide, and what advantages the employment of aluminium or of sodium and potassium amalgam as precipitants presents over that of zinc upon a working scale.

C. The Extraction of Gold by the Formation of Alloys from which the Gold is Obtained by Parting

This method of gold extraction coincides as regards the formation of the alloys with the already described smelting processes, and as regards the separation of gold therefrom with gold parting to be described presently.

IV. The Electrometallurgical Extraction of Gold

Electrolytic methods have so far only been used to advantage in separating gold from its alloys, as will be described under the head of parting.

Methods of gold extraction from ores, such as have been proposed by Cassel and Barker, have never come into use. Cassel's [1] method consisted in treating the ore in a revolving drum with a solution of salt, through which an electric current is passed. The chlorine thus set free was supposed to dissolve the gold, whilst the acids formed by secondary reactions were neutralised with lime.

Barker's method, which was in use for a short time only at Curra Rossi, in Hungary, consisted in amalgamating ores crushed between rolls in revolving cylinders, the greater part of the amalgam produced being then separated from the residues by discharging the mass from the cylinders on to large tables, and finally the rest of the amalgam was collected on amalgamated plates by the aid of the electric current.

[1] *Dingler's Journal*, vol. 254. p. 296.

Molloy's hydrogen-amalgam method similarly consisted in keeping the surface of mercury used in amalgamation bright by means of an electric current; it has never come into successful use.

Parting

As the greater part of the gold produced carries silver and the greater part of the silver carries gold, the parting of gold from silver in the alloys of these metals is an important metallurgical process. These gold-silver alloys often contain, besides gold and silver, other metals that affect the properties of the first-named injuriously, such as lead, bismuth, tin, antimony and arsenic, and these must, therefore, be removed as far as possible before parting, by means of cupelling or refining. It is, however, but rarely possible to get rid of these substances down to the last traces before parting. The process of parting has, therefore, for its object the removal of the last traces of foreign elements in addition to separating silver and gold.

Parting can be performed in the dry way, in the wet way, and electrolytically.

The dry method of parting depends on the conversion of the silver into sulphide or chloride, whilst gold is attacked by neither sulphur nor chlorine at high temperatures.

The wet method depends on the solubility of silver and the insolubility of gold in nitric acid and in boiling concentrated sulphuric acid.

The electrolytic method depends upon the property of silver to pass from anodes of gold-silver alloys to the cathode, whilst the gold remains at the anode, when a suitable current density and electrolyte (acidulated solution of nitrate of silver) are employed.

The methods of parting that are preferred nowadays are parting by means of hot concentrated sulphuric acid, known as *refining*, and parting by means of electrolysis, the latter method having replaced refining at several works.

A. Parting in the Dry Way

The methods of gold parting in the dry way are by means of sulphide of antimony, by litharge and sulphur, or by sulphur alone, by means of salt (cementation), and by Miller's chlorine method.

Of these, the last-named alone is still in use; the other methods were often used in former times, but have been replaced universally by wet and electrolytic processes, and therefore only possess historic interest.

PARTING BY SULPHIDE OF ANTIMONY OR BY *GUSS UND FLUSS*

This method depends upon the fact that when a gold-silver alloy is melted with sulphide of antimony, the silver combines with the sulphur, whilst the gold alloys with the antimony.

From this alloy, antimony can be removed by oxidation or volatilisation by the employment of a high temperature, whilst the silver can be recovered from the sulphide in various ways, most readily by treatment with lead, with the addition of iron. It is not, however, possible to obtain by a single fusion pure antimonial gold and sulphide of silver, the latter being known as *plachmal*. On the contrary, it is necessary to repeat several times the fusion of the antimonial gold with fresh quantities of sulphide of antimony in order to remove all the silver from the former. On the other hand, the *plachmal* still carries gold and contains undecomposed sulphide of antimony; it is remelted several times in order to remove the gold as far as possible from it in the form of antimonial gold. Small quantities of gold, however, remain with the *plachmal*, and collect in the silver reduced from it; to separate these, this silver is parted by means of nitric acid.

This process can only be applied when the alloy to be parted contains not less than 50 per cent. of gold. It used to be frequently employed, and has been described exhaustively by Schlüter in 1738.

Up to the year 1846 it was practised at the mint at Dresden, where alloys containing 64 per cent. of gold were parted by it. These alloys[1] were there melted in Hessian crucibles in an air furnace with three times their weight of sulphide of antimony. As soon as the molten mass commenced to emit sparks, it was poured into either a conical iron mould or an old crucible; in these vessels a lump of gold alloyed with antimony formed at the bottom and above it the *plachmal*. The gold was then melted in the same way a second time with twice its weight, and a third time with its own weight of sulphide of antimony. If it still retained notable quantities of silver, it was remelted with twice its weight of sulphide of antimony until the gold in the alloy had attained the desired degree of fineness.

The alloy, containing about 40 per cent. of antimony, was then melted in a covered Hessian crucible, coated internally with borax. As soon as fusion had occurred, air was blown on to the surface of the bath of metal with a bellows, whereby the antimony was oxidised and volatilised as antimonious oxide. When the antimony had been

[1] Percy, *Silver and Gold*, p. 373.

removed the gold solidified; nitre and borax were added, and the temperature raised up to the melting point of gold, when it was poured.

The *plachmal* was melted in a Hessian crucible with iron, lead and fluxes, producing work-lead and regulus.

The work-lead was cupelled and the auriferous silver thus obtained treated with nitric acid. The silver was precipitated from the solution by means of copper and melted with carbonate of soda. The residual gold was melted with borax and nitre.

The regulus, which still contained considerable quantities of silver, was smelted together with mint *sweep*.

Parting by Means of Sulphur and Litharge

This method, known as the *Pfannen-schmied* process, has for its object the concentration of gold in a gold-silver alloy to such an extent that it can advantageously be submitted to parting by nitric acid. It depends upon the transformation of the silver of the alloy into sulphide of silver by means of sulphur, and the decomposition of a portion of this sulphide of silver by litharge into sulphide of lead, lead and silver, which latter collects the particles of gold scattered through the mass, and, together with the lead, forms a mass of *bottoms* at the bottom of the crucible, whilst the sulphides of lead and silver form the *plachmal*. The latter is first freed from gold by means of repeated fusions with litharge, and then smelted with iron, producing work-lead and an argentiferous regulus or matte.

This lengthy and complicated process was formerly in use at Oker, where it has been replaced by parting by sulphuric acid.

The *Blicksilber*,[1] which contained 0·26 to 1·38 per cent. of gold,[2] was first granulated, mixed whilst still damp with $\frac{1}{8}$ of its weight of sulphur, and charged in small quantities into a blacklead crucible. By gradually heating the latter the sulphur was first caused to frit and then to melt with the silver, which was thereby converted into sulphide, whilst the gold remained as metal, finely divided and disseminated through the molten mass of sulphide of silver. In order to obtain *bottoms* consisting of gold and silver, after the fusion was complete, litharge to the extent of $\frac{1}{16}$ was sprinkled in small quantities upon the molten mass, thus reducing a portion of the sulphide of silver to metal with the evolution of sulphur dioxide. The lead

[1] See *ante*, p. 580.

[2] Jordan, *Journ. f. Pract. Chem.* 1836, 9, pp. 74–84. Lampadius, *Grundriss einer allgemeinen Hüttenkunde*, Göttingen, 1827, p. 269.

reduced from the litharge in part displaced more silver from the sulphide and in part alloyed with the separated silver. The silver-lead alloy thus produced took up the disseminated gold and settled down to the bottom of the pot, whilst the sulphides of lead and silver formed a layer of *plachmal* above it. After the crucible had been allowed to cool in the furnace, the alloy was separated from the *plachmal* by breaking off the latter, the lead was cupelled off and the residual silver-gold alloy parted by nitric acid.

The *plachmal* still retained gold, to extract which it was melted four or five times with sulphur and litharge. The *bottoms* containing gold thus produced, were melted with litharge until their gold content was sufficient for a satisfactory parting with nitric acid; as they contained much lead in consequence of this treatment, they had to be cupelled before being parted.

The *plachmal*, from which the gold had thus been removed, was smelted in graphite crucibles with ¼ its weight of iron, producing work-lead and regulus. This regulus was roasted in a reverberatory furnace and smelted in graphite pots with 20 per cent. of iron and 30 per cent. of litharge, producing work-lead and a second regulus. The latter was smelted in a graphite crucible with various silver-bearing residues and broken up old crucibles, forming work-lead and a third regulus, the operation being known as *Krätzschmelzen*. The third matte was smelted with various by-products containing lead and silver in low blast furnaces (*Krummofen*), producing work-lead, slag and a matte, which still contained certain amounts of lead and iron, this operation being called *Krätzfrischen*. This last matte was calcined and added in the previous operation. The various work-leads were cupelled and the auriferous *blicksilber* so obtained was parted with nitric acid.

Parting by Sulphur Alone

The object of this method of parting, which is referred to by the monk Roger[1] as early as the 11th century, is to produce alloys of silver rich in gold from silver poor in gold.

The silver was granulated, mixed while damp with ⅛ its weight of sulphur, and the mixture transferred to a crucible in which it was heated gradually up to its melting point. Auriferous silver was then added to collect the gold, and the molten mass was poured into a conical mould. An alloy of gold and silver collects at the bottom, and above it the sulphide of silver (*vlachmal*). If the alloy was still

[1] An Essay upon various Arts in three books, by Theophilus, called also Rugerus, Priest and Monk. Translated with notes by Robert Hendrie, 1847, pp. 316–319.

too poor to be advantageously parted by nitric acid, it was treated again with sulphur in the same way. The enriched alloy was melted with lead and cupelled, and then parted by nitric acid. The *plachmal* was melted with iron to recover the silver.

This process was in use in the last century at the St. Petersburg mint.[1]

Instead of adding silver to collect the disseminated particles of gold, iron has also been employed. This separated out some silver from the *plachmal* with the formation of sulphide of iron; the silver collected the gold as before.

In the 16th century, gold was separated from silver at the Delhi[2] mint by melting the alloy with copper and then with sulphur. The alloy was melted three times with copper and then three times with sulphur, whereby the gold was separated. The argentiferous copper thus produced was converted into a lead-silver-copper alloy from which the silver was extracted.

Quite recently sulphur has been used successfully by Roessler to remove the copper from silver-gold alloys before submitting these to wet parting.

Parting by Means of Salt or "Cementation"

Parting by means of common salt, known as *cementation*, depends upon the conversion of the silver of the alloy into chloride of silver by heating with salt and clay, or salt and green vitriol or alum and sand, whilst the gold remains unchanged. Chloride of silver was produced both by the direct action of salt upon silver (H. Rose, Winkler, Plattner) and by the action of the chlorine, metallic chlorides and hydrochloric acid, which may be formed in the process. The chlorine might have been produced both by the action of sulphur trioxide upon salt and by the decomposition of hydrochloric acid in the presence of air by means of contact action (Oxland), whilst the hydrochloric acid might have been formed by the action of sulphuric acid upon salt, or by that of silica in the presence of water vapour. The chloride of silver was absorbed by the sand or the brickdust used in its place.[3]

Cementation is one of the oldest metallurgical processes, and has been described by Geber, Albertus Magnus, Beringuccio and Agricola.

[1] Crells' *Chemische Annalen*, 1797, Part I. p. 115.

[2] Percy, *Silver and Gold*, p. 374.

[3] For a fuller account of the reactions during cementation, see Percy, *Silver and Gold*, p. 384. Boussingault, *Ann. Chem. et Phy.*, 1833, 54, pp. 253–263. *Poggendorf. Annal.*, 32, 99 (1834).

It is probably no longer in use anywhere. It was used as recently as 1833 in Santa Fe de Bogota, Columbia, S. America, to remove so much of the silver from native gold as to fit it for coinage.

According to Boussingault[1], the argentiferous gold, which contained up to 35·07 per cent. of silver, was granulated, and heated to redness in porous clay pots filled with a mixture of 1 part of salt and 2 parts of brick-dust. After heating for 24 to 36 hours, the operation was complete. The gold was found in grains in the cementing powder, whilst the silver, in the form of chloride, had been absorbed by the latter. The gold was separated from the cementing powder by washing, and was found to be 87·5 to 91·7 per cent. fine. The silver was extracted from the cementing powder by amalgamation with ten times as much mercury as it contained silver, together with one-tenth of its total weight of common salt. The amalgam so obtained was retorted and yielded silver that only retained a few thousandths of gold.

Parting by Chlorine Gas or the Miller Process

This method depends on the property of chlorine gas, of converting the silver contained in molten gold-silver alloys into chloride, whilst not attacking the gold. When chlorine gas is passed through such alloys, the base metals present (lead, arsenic, antimony, bismuth, copper) are the first to be converted into chlorides, and such of the latter as are volatile (lead, arsenic, antimony) are vaporised. The process can therefore also be used for the removal of base metals from gold-silver alloys, before parting the latter. Hitherto it has found only a limited application for getting rid of base metals and of silver from argentiferous gold.

The method was proposed in 1838 by Lewis Thompson[2] but was not practically applied. It was not till 1867 that it was introduced by Francis Bowyer Miller with various important improvements (amongst which may be reckoned the fusion of the alloy under a cover of borax, and the treatment of the auriferous chloride of silver) at the Sydney mint[3] on a large scale for refining and desilverising gold, and it has therefore received the name of Miller's process.

Besides the Sydney mint, it has also been employed in the London mint by Roberts-Austen for refining gold.[4]

The alloy is melted in clay crucibles, enclosed within plumbago crucibles so as to avoid loss of metal in case of the crucible cracking. The clay crucibles are glazed internally with borax to prevent the

[1] *Loc. cit.* [2] Percy, *Silver and Gold*, 1880, p. 402. [3] *Ibid*, p. 405, *et seq.*
[4] Eissler, *The Metallurgy of Gold*, London, 1889, p. 257.

chloride of silver penetrating into them. Through the loosely fitting clay cover chlorine gas is passed into the molten alloy by means of a clay pipe, reaching almost to the bottom of the crucible. The crucibles are heated in air furnaces. The chlorine gas is generated from oxide of manganese and hydrochloric acid in a stoneware vessel heated on a waterbath. The generator is furnished with a stoppered aperture, by means of which the necessary materials can be charged, an escape pipe for the chlorine gas, and a long safety tube reaching to the bottom of the vessel. The upper end of this safety tube opens into a vessel into which the fluids in the generator can be forced by a high pressure inside the generator. It also admits of the pressure being observed by means of the height of the fluid column, the

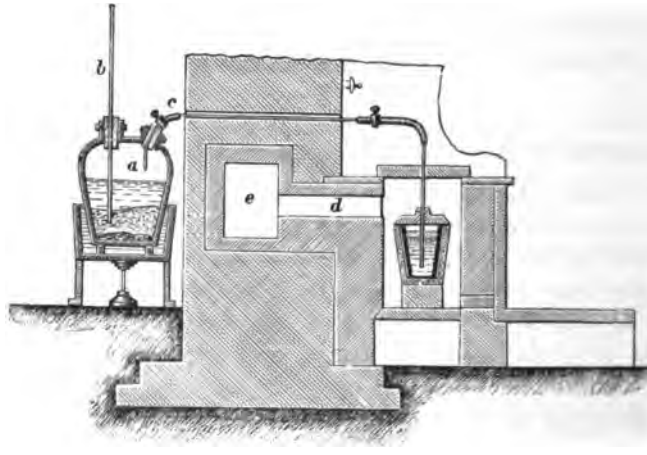


FIG. 560.

pressure being necessary in order to force the chlorine gas into the molten alloy. The hydrochloric acid requisite for generating the chlorine, can also be introduced through this safety tube.

The arrangement of a plant for parting by chlorine gas is shown in Fig. 560.

The inner crucible is made of white, fine clay; it is glazed internally by being filled with a boiling solution of borax in water, which is allowed to stand in it for some ten minutes, after which it is poured out, and the crucible allowed to dry. The glaze forms as soon as the crucible is heated in the course of the process. A clay tube (that used in London was 22 inches long, $\frac{1}{2}$ inch outside, $\frac{5}{16}$ inch inside diameter) passes through the loose cover, which is also pierced by several apertures to allow the fumes to escape.

The chlorine generator is shown at *a*, *c* being a leaden tube for conveying the gas, *b* is the glass safety tube 8 to 10 feet long, terminating at its upper end in a vessel not shown in the figure, to receive the fluid driven up when the eduction tube is closed. A column of liquid of 16 to 18 inches in height balances 1 inch of gold in the crucible. The tubes are inserted into the generator through indiarubber stoppers. The chlorine eduction tubes are coupled together by means of indiarubber tubes or flanges; they can be closed by compression clamps. The larger opening for the introduction of the requisite materials is not shown in the figure; it is closed by means of a leaden plug covered with indiarubber. The chlorine generator has a capacity of 26 gallons, and stands in a water-bath. On the bottom of the former there is a layer of small pieces of quartz upon which rests the oxide of manganese, in quantities of 90 to 100 lbs., broken into small pieces, say about ¼ inch cube. At the Sydney mint the chlorine passes from the generator into a leaden main that serves a row of furnaces, and from which two branches lead to each crucible, one of the two being used for a reserve tube.

The gold that is thus parted at Sydney contains silver and small quantities of lead, arsenic and antimony, very small proportions of which suffice to render the gold unfit for coinage; the average proportion of silver is 5 per cent.

The process is there conducted as follows:—The gold is charged into the crucible, previously heated to redness, in two ingots of 740 ounces each, and is slowly heated to the melting point; as soon as it is fluid 2 to 3 ounces of molten borax are added. The clay pipe, the end of which has first been heated, is then lowered into the molten metal, and the chlorine admitted. The volatile chlorides of the base metals contained in the gold are immediately evolved in the form of vapours, which appear denser the more lead they contain. They disappear as soon as the base metals have been removed, the chlorine now combining with the silver. If there is only a small quantity of the latter metal in the gold, dark vapours and a brownish yellow flame then make their appearance. As soon as the latter produces a reddish or brownish deposit upon a clay tube held in it (which occurs in the case of gold containing 10 per cent. of silver in 1 to 1½ hours), the operation of parting is completed. The crucible is lifted out of the furnace, allowed to cool for a few minutes, and the still fluid chloride of silver is poured off into previously heated moulds, after which the crucible is inverted and the solidified gold drops out. It is washed with salt solution to remove adhering

chloride of silver and re-melted. Its fineness is then 991 to 997 per mil. By repeating the operation yet more silver can be removed. Of the gold present in the alloy, 98 per cent. is collected in the fine gold, whilst 2 per cent. passes into the chloride of silver.

The latter is first freed from gold and then reduced. The former process was at first performed by a fusion with metallic silver, which, when molten, collected the gold and formed a metallic mass at the bottom of the crucible. This process, which only removed the gold imperfectly, has been replaced by melting the chloride of silver with carbonate of soda under a borax cover, according to the method suggested by Leibius.[1] In order to avoid loss of metal through ebullition, the chloride of silver was first covered with a layer of borax to a depth of 0·4 inch, and then carbonate of soda (about 1 lb. to 16 lbs. of chloride of silver) was sprinkled in small quantities upon the borax cover. By treating it twice in this way the gold is said to be pretty completely removed. The gold is obtained as an alloy with a portion of the silver.

The silver is extracted from the chloride electrolytically by a method also proposed by Leibius. Plates of zinc or silver are employed as electrodes, the electrolyte consisting of a solution of chloride of silver dissolved in salt or in chloride of zinc; the silver obtained is melted in graphite crucibles. If the gold to be parted contains copper the latter passes, for the most part, into the silver.

The argentiferous residues from the above processes are ground in Chilian mills and then amalgamated. The loss of gold by the above process is given by Miller for 100,000 parts of alloy containing 89 parts gold, 10 parts silver, 1 part base metals, as 19 parts = 0·21 per mil, and of silver for the same amount of alloy as 240 parts = 24 per mil.

The method of parting by chlorine is inferior economically to that of parting by sulphuric acid and by electrolysis.

B. Parting of Gold by the Wet Method

The wet methods of gold parting are parting by means of nitric acid or *inquartation*, and parting by sulphuric acid or *refining*. Aqua regia is only used as an auxiliary in parting by sulphuric acid. Parting by nitric acid is now only employed in exceptional cases, on account of the high price of this acid.

[1] *Dingl. Journ.*, vol. 197, p. 55.

PARTING BY NITRIC ACID

According to Albertus Magnus this process was in use at Goslar as early as 1433. It was universally employed formerly till it was supplanted in 1802 by the cheaper method of parting by sulphuric acid, introduced by d'Arcet. It is now used in but few places, *e.g.*, the mints of Philadelphia and San Francisco.

It is called *inquartation* because it used to be held that for its success the proportion of gold in the alloy should not exceed $\frac{1}{4}$. Pettenkofer has, however, shown that parting can be performed successfully when the proportion of gold to silver in the alloy is $1 : 1\frac{3}{4}$. If more gold than this is present, some silver remains with the gold. Alloys too rich in gold must therefore be melted with the requisite quantity of silver before being parted.

If the alloy is too poor in gold, parting is indeed possible, but entails a heavy consumption of nitric acid. Poor alloys were therefore formerly enriched by treatment with sulphur and litharge (see page 844). Parting is performed in vessels of glass, stoneware or platinum.

The alloy may not contain any metal other than silver and gold, except palladium, copper and lead. When tin, antimony and arsenic are present, it must be refined before being parted, by fusion with oxidising agents or by cupellation with lead.

The alloy is granulated and then treated with nitric acid, whereby the silver is dissolved whilst the gold remains in the residues. By repeated treatment of the latter with nitric acid or with boiling concentrated sulphuric acid, the silver still remaining in it may be removed down to a very small residual quantity.

The nitrate of silver solution may be evaporated to dryness to form lunar caustic, or this salt may be ignited with the production of metallic silver, or the solution may be precipitated by means of common salt, forming chloride of silver, which can then be reduced.

Percy[1] describes as follows the process of parting by nitric acid as practised by Johnson, Matthey and Co., of Hatton Garden, London. The gold, refined if necessary, is melted in graphite crucibles with so much silver that an alloy containing gold and silver in the proportion of 1 : 3 is produced. The granulated alloy is treated with nitric acid in vessels of stoneware or platinum.

The platinum vessels have a capacity of about 9 gallons, and are fitted with stoneware lids; their charge is 800 ounces of granulated metal; each vessel is heated by a separate furnace. The acid

[1] *Op. cit.*, p. 446.

vapours that escape on heating are condensed as far as possible in suitable chambers, the uncondensable part being conveyed into the ash-pits of the furnaces. The nitric acid employed has a specific gravity of 1·4, and is diluted with an equal volume of water. The granulated metal is boiled three times with nitric acid. The first boiling lasts 4 hours; the solution is then poured off, and fresh acid is poured on, which is boiled for 3 hours, to be followed by a third boiling of 2 hours' duration with fresh acid. The last acid takes up but little silver, and is accordingly used for dissolving a fresh charge of granulated metal. The residual gold is washed with hot water, dried and melted in graphite crucibles; the melted gold is 998 per mil fine.

Chloride of silver is precipitated from the solution of nitrate of silver by means of salt. It is washed with hot water and then treated with granulated zinc and very dilute sulphuric acid, whereby the silver is separated as metal. It is washed, dried, and melted, and is then 998 parts per mil fine.

In the mints of Philadelphia and San Francisco the parting by nitric acid is combined with that by sulphuric acid, this method having been introduced in 1866 by A. Mason.[1] The alloy is so adjusted as to contain 100 parts of gold in 285 of alloy. It is first treated with nitric acid until the silver contents of the residue are reduced to 6 per cent. The latter is then boiled twice with concentrated sulphuric acid, whereby gold 998 parts per mil fine is obtained. Chloride of silver is precipitated from the nitrate solution by means of salt, and is reduced to metal by zinc and sulphuric acid.

The bullion received at the mint is first refined, if it is impure.[2] The gold is melted in Hessian, the silver in blacklead crucibles. Antimony is removed from the silver by stirring the molten metal with an iron rod, with the addition of some nitre; by this means the antimony is very rapidly removed, generally in two to three minutes. Tin is removed from silver and gold by the addition of salammoniac or potash, iron and sulphur by a mixture of nitre and sand, lead and arsenic by boneash and nitre.

The gold and silver are melted together for inquartation in blacklead crucibles, and the alloy is granulated. The granulations are treated with nitric acid in pots of glazed earthenware set in a water-bath heated by steam. The pots are between 21 and 24 inches in diameter, and 21 to 22 inches deep, and are provided with handles. The charge is 135 lbs. of granulations, and 125 lbs. of nitric acid of 40° B.; the pots are not covered. To keep the granulations from

[1] Egleston, *op. cit.*, vol. ii.; p. 698. [2] *Ibid.*, p. 700.

clotting together they are stirred every 20 minutes. After boiling for 12 hours, and settling for another 12, the silver nitrate solution is diluted with water and drawn off by a gold syphon; 75 lbs. of fresh acid are then poured on to the residue, heated for 12 hours, allowed to settle for 12, and drawn off again. As it contains but little silver this acid is employed to dissolve a fresh batch of granulations.

The residual gold is washed on a filter with hot water, and boiled twice with concentrated sulphuric acid. This boiling is performed in cast-iron pots, 22 inches in diameter at the top and 12 inches deep in the centre. They are heated by means of anthracite coal, and are covered with conical leaden hoods terminating above in a leaden tube; in order to be able to stir the contents the hood is provided with an opening, which can be closed by a piece of sheet lead. The gold is boiled twice for 1½ hours with sulphuric acid of 66° B., each charge of sulphuric acid weighing 32 lbs. The pot must be stirred every 10 or 15 minutes, to keep the gold from agglomerating. After the second boiling the gold is 996 to 998 per mil fine; by a third boiling it can be brought up to 999·5 fine. The gold is thoroughly washed on a filter, dried, and melted.

Sulphate of silver is precipitated from the solution by diluting it.

The silver nitrate solution is treated in wooden tanks with salt solution, which precipitates the silver as chloride; the latter is filtered off, washed with cold water, and then reduced by granulated zinc. The reduction is performed by the addition of sulphuric acid in lead-lined tanks. For every 3 parts of silver chloride, 1 part of zinc and 1½ parts of sulphuric acid of 60° B.[1] are consumed. The silver is washed with hot water on cloth filters, pressed in hydraulic presses, dried in iron trays, melted and cast into bars. The gold is dried without being pressed, melted, and cast into bars.

PARTING BY SULPHURIC ACID, OR REFINING

This process was first employed upon a working scale by d'Arcet in Paris in 1802. It depends on the solubility of silver in boiling concentrated (66° B.) sulphuric acid, in which gold is insoluble. The solution of silver takes place in accordance with the following equation:—

$$Ag_2 + 2H_2SO_4 = Ag_2SO_4 + SO_2 + 2H_2O.$$

The silver sulphate thus formed dissolves in the excess of acid. The residue rich in gold is treated in various ways to obtain fine gold, whilst the silver is precipitated as metal from the solution of the sulphate.

[1] Percy, *op. cit.*, p. 444.

Refining is applicable to alloys of all degrees of fineness, and has the advantage of cheapness over all other forms of gold parting, except electrolysis, since by its means alloys containing 0·05 per cent. of gold, and even less, can be parted with advantage; for this reason it has replaced the older methods of parting, and is still extensively used. A rival method has, however, arisen in electrolytic parting, which has already displaced it in some of the larger works; in smaller works it will probably continue to hold its own.

According to Pettenkofer[1] refining gives the best results, and yields the finest gold, when alloys with 19 to 25 per cent. of gold are operated on. When the proportion is higher the sulphuric acid does not readily penetrate the alloy, whilst when it is lower it becomes difficult to separate the silver from the gold in the last stages of the process. It is, however, not possible to remove the last traces of the silver even by repeated treatment of the alloy with sulphuric acid. If the gold is required quite fine and free from silver, it has to be treated by special methods.

The action of hot sulphuric acid upon the components of the alloy is as follows, according to a communication of Roessler to Percy.[2]

The silver, as already stated, is converted into sulphate, the latter being soluble in ¼ its weight of boiling sulphuric acid of 66° B. (One part of silver sulphate is soluble in 180 parts of cold, and 30 parts of boiling sulphuric acid of 10° B., in 20 parts boiling acid of 20° B., in 4 parts of cold and 0·25 of boiling acid of 66° B.)

According to theory, 216 parts of silver require for their solution 196 parts of sulphuric acid; actually, 2 to 2½ parts of acid are required to 1 part of silver. An excess of acid is required to keep the sulphate of silver in solution, to promote energetic solution of the silver, and to convert any other metals contained in the alloy into sulphates. Platinum, osmium and iridium remain with the gold, whilst palladium is somewhat attacked by sulphuric acid. In the presence of large quantities of silver even palladium is not attacked.

Copper is converted into sulphate by the sulphuric acid. This salt is but feebly soluble in concentrated sulphuric acid, and remains for the most part as a white anhydride with the gold. As this anhydride encrusts portions of the alloy, the solution of the latter is rendered more difficult, and needs a larger quantity of acid. When the hot silver solution cools, the small quantity of sulphate of copper dissolved in it separates out completely. According to Roessler, alloys containing more than 10 per cent. of copper should be freed

[1] *Dingl. Journ.*, vol. 104, p. 118. [2] *Op. cit.*, p. 458.

from the latter before being parted. The best process for this purpose is that of Roessler, to be given below.

Lead softens and its particles cake together at the temperature required for parting; it can therefore only be converted with difficulty into sulphate by boiling concentrated sulphuric acid. When alloyed with silver it is more readily converted into sulphate. As lead sulphate is but slightly soluble in hot sulphuric acid, and still less in cold, it separates out with the gold as a white powder. When the solution is diluted with water the whole of the lead dissolved in the acid is precipitated.

Tin is in part dissolved, and in part remains with the residue, which it colours purple.

Zinc is with difficulty converted by the hot concentrated acid into sulphate, which is insoluble in the concentrated acid, and remains with the residual gold.

Iron, when cast-iron pots are used, is gradually converted into ferrous sulphate; this, in its anhydrous form, is insoluble in the concentrated acid, and remains with the gold. Grey cast-iron is attacked a good deal more strongly than white; experience has shown that iron pots are much less attacked when the alloy under treatment contains copper.

The complete process of parting by sulphuric acid embraces the following operations:—

1. The preparation of an alloy suitable for parting, and its granulation.
2. The solution of the silver of the alloy by means of sulphuric acid.
3. Obtaining the gold from the auriferous residue.
4. Treatment of the silver sulphate solution for the extraction of the silver.

1. *The preparation of an Alloy suitable for Parting, and its Granulation*

Impurities, small quantities of which affect injuriously the malleability of gold and the valuable properties of silver, such as lead, bismuth, tin, antimony, arsenic and tellurium, should be removed as far as possible before parting, by melting the alloy with oxidising agents, such as air, nitre or sulphate of silver. It is, however, impossible to prevent very small quantities of the above substances from remaining behind in the alloy, and these have to be removed from the gold or silver after parting.

The substances are removed from gold-bearing silver before parting in the manner described under silver refining. From argentiferous gold they may be removed by fusion with nitre. It is better to melt the gold with its corresponding quantity of silver, and to treat the alloy like auriferous silver.

Copper only acts injuriously in that it forms anhydrous copper sulphate, which in part incrusts the alloy and makes the parting more difficult, besides increasing the consumption of acid. If the copper in the alloy exceeds 10 per cent. parting can no longer be conducted with advantage; in this case the copper must be partially or completely removed. The proportion of copper may be decreased by melting the alloy with silver free from copper, but the costs of parting are thus increased again.

It is therefore better to remove the copper by Roessler's method. This consists in melting the alloy with excess of sulphur in a crucible, whereby the copper and a portion of the silver are sulphurised; air is then blown upon the molten mass, which reduces the greater part of the sulphide of silver, whilst the copper and a little silver remain combined with sulphur. The alloy of gold and silver collects at the bottom of the pot, and above it a layer of sulphide of copper still containing a portion of the silver. By melting this layer in a second crucible and directing an air-blast into it when molten, an alloy of copper and silver is produced from which the silver can readily be recovered by electrolysis, by treatment with dilute sulphuric acid, or by smelting with lead.

The sulphur dioxide produced in this process can be conveyed to a condensing chamber by means of a Korting's injector, and passed through aqueous solutions containing copper or argentiferous copper. The copper is gradually converted into sulphate, whilst any silver contained in it remains behind. At the parting establishment at Frankfort-on-the-Maine, 660 lbs. of metallic sulphides are treated as above in a graphite crucible heated in an air-furnace, using coke as fuel.

Of the metals of the platinum group, osm-iridium and iridium render gold brittle, whereas platinum only affects the malleability of gold when present in large proportion, but causes silver to be retained by the gold.

At the New York mint,[1] gold containing osm-iridium is melted in crucibles with 4 to 5 times its weight of silver. The molten mass is allowed to stand at rest for 15 minutes in the furnace, when the heavy platinoid metals settle at the bottom of the crucible. The

[1] Egleston, *op. cit.*, p. 751.

alloy is then poured off till it begins to run pasty. The residue consists of silver containing the whole of the platinoid metals; any gold contained in it is removed by melting again with silver and allowing the platinoid metals to settle as before.

As these operations increase considerably the cost of parting, the platinoid metals which remain with the gold during the process of parting are removed afterwards by means of aqua regia or by electrolysis. Platinum alone may be removed from gold by fusion with nitre, when it goes into the slag as platinate of potash.

After the alloy has been purified, it is granulated; it may be noted that in some works in the United States, the alloy is not granulated but is parted in the form of thin slabs.

If the alloy does not need purifying, it is merely melted and granulated. In many cases however the alloy does not possess the composition requisite for advantageous parting; in places where alloys rich in silver and others rich in gold are available, these are therefore melted together in such proportions that the resulting alloy shall contain them in a ratio suitable for parting. For instance, at Kremnitz, in Hungary, the alloys are made up to contain $\frac{9}{10}$ silver and $\frac{1}{10}$ gold.

At the New York mint[1], the mixing of gold and silver, the so-called inquartation, is so arranged that the alloy shall contain from 2 to 4 parts of silver according to the amount of copper present, for each part of gold, and that the proportion of copper shall if possible not exceed 6 per cent.; under no circumstances is it allowed to exceed 10 per cent. of the weight of the alloy. At the assaying and refining works at San Francisco, argentiferous gold bars from California used to be so inquartated as to contain 2 parts of gold to 3 of silver. The alloys thus produced are directly granulated.

Refining the alloys, inquartation and fusion for granulation are usually performed in graphite pots heated in an air furnace. Only the refining of auriferous *blicksilver* is often conducted, as explained under Silver, in reverberatory furnaces or, in rare instances, in muffles.

The air furnaces are fired either by coke or by coal-gas. They are best made circular in horizontal section, and leaving but little space between the crucible and the furnace walls for the fuel. The height from the floor to the mouth is about 3 feet, that of the shaft body above the firebars 18 inches. They are preferably constructed with outer plates of cast iron surrounding the furnace body, which is built of firebrick.

The capacity of the crucible ranges up to about 20,000 ounces of

[1] Egleston, *op. cit.*, p. 750.

alloy. For example, the coke-fired air furnaces at Lautenthal take charges of 10,250 ounces of auriferous blicksilver for refining, at the Schemmitz mint 16,000 ounces for inquartation and granulation, whilst in the New York mint charges of about 2,300 ounces are granulated.

The granulation of the alloy is performed by ladling it out from the reverberatory furnace or crucible and pouring it in a thin stream into cold water kept in agitation by means of a wooden stick. The water is contained in a copper pan. In order to facilitate the stirring, this pan has a loose-lying movable false bottom with a central hole, above the true bottom. The granulations drop through this opening into the true bottom of the pan. The consumption of coke amounts to 40 to 60 per cent. of the weight of alloy.

Before being treated with sulphuric acid, the granulations are dried on heated iron plates or in copper trays.

2. *Solution of the Silver in the Alloy by means of Sulphuric Acid*

The silver in the alloy, which is either in the form of granulations or of thin slabs, is dissolved, as a rule, in cast-iron pots. Porcelain vessels are only employed when very small quantities of bullion have to be parted. Platinum vessels used formerly to be employed, but on account of their high price and of the gradual action of the sulphuric acid upon them, they have been replaced by cast-iron pots.

Cast-iron pots are best made of white iron, as being less attacked than gray by the acid; the same effect is produced by a high proportion of silicon or phosphorus in the iron. If kept from the air, such pots may last for several years. As the presence of copper diminishes the action of the acid upon the iron, in some works copper is thrown into the pots during parting. The pots are made large enough to hold 13,000 to 16,000 ounces of bullion. For instance, the charge at Freiberg is 12,000 to 16,000 ounces, at Lautenthal about 6,400 ounces, at Kremnitz 8,000, at Balbach in Newark 8,000, at the New York United States mint 3,600 to 4,800 ounces, according to the fineness of the alloy. The pots at Freiberg are 40 inches in diameter and 40 inches deep, those at Kremnitz are of the same size, those at Lautenthal 33 inches deep and 33 inches in diameter, at New York 45 inches in diameter and 26 inches deep. The castings are about $1\frac{1}{2}$ to $1\frac{3}{4}$ inches thick.

Below the pot is a vessel or tray of cast iron, so disposed as to catch the fluid contents of the former in case it should crack, and to conduct them to a leaden tank sunk in the floor in front of it.

The setting of the pots at Lautenthal, the fireplaces and flues, as well as the arrangement for catching any fluid that may escape, are shown in Figs. 561 and 562.

In these *A* is the dissolving pot, *d* the cast-iron plate for conducting any escaping fluid to the tank *S*, *B* is a pot for receiving the silver solution produced in *A*, *P* is a small pot for boiling up the gold residue.

The pots are covered with leaden hoods or lids, or with wooden lids lined with lead, in which there are openings for introducing the

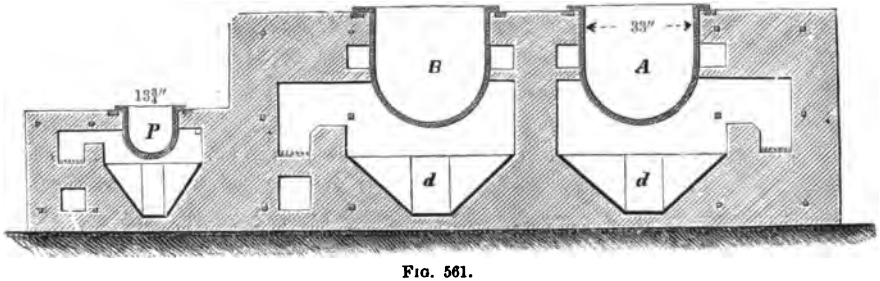


Fig. 561.

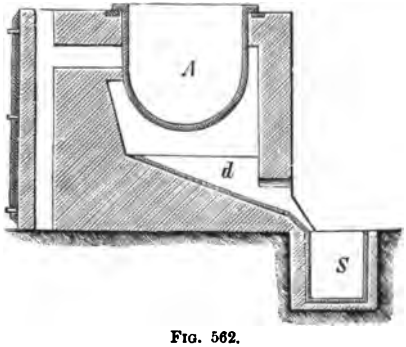


Fig. 562.

bullion and the acid, and a leaden tube for leading away the sulphur dioxide. The opening for introducing the alloy serves also for stirring up the contents of the pot, for ladling out the silver solution and for removing the gold.

At the New York mint, the pots are covered with hemispherical leaden hoods strengthened by internal iron ribs; they have also the above-named opening, and are connected by a water seal with a leaden pipe for carrying off the fumes. The acid vapours evolved during parting pass first to a condensing chamber, in which any particles of sulphate of silver that are carried over, may be deposited,

and thence into various arrangements for rendering the sulphur dioxide innocuous. It may be converted into sulphuric acid in lead chambers, or collected in lead towers filled with wet coke, as at New York, or employed in Roessler's apparatus for dissolving the copper from silver-copper alloys, as at Frankfort, or led into a leaden tower filled with scrap iron, down which water trickles, as at Freiberg.

In this latter process, devised by Winkler, a solution is obtained containing ferrous sulphate and hyposulphite, which, on boiling with steam, is converted into ferrous sulphate, with the formation of sulphur and sulphur dioxide, which latter is led back into the tower.

The vapours containing sulphur dioxide and sulphuric acid can only be allowed to escape directly into stacks, when there is no fear of complaints on the score of nuisance from the neighbours of the parting establishment.

Porcelain vessels are used when small lots of bullion only are treated, *e.g.*, at Oker in the Hartz, where the charge amounts to 190 to 225 ounces. The operation in these vessels is cleanly, and entails only very small mechanical losses.

The arrangement of such a porcelain dissolving vessel as used at Oker, is shown in Figs. 563 and 564.

The porcelain pot is shown at *a*; it is 13·4 inches high, 13·4 inches in diameter at its widest part, 11 inches at the bottom, and 9·25 inches at the top, and takes a charge of 200 ounces. To keep it from cracking, it is enclosed in a netting of iron wire, and is coated with a mixture composed of clay and hammerscale. It is set in an iron frame *b*, with handles *c*, which in its turn is placed inside the cast-iron pot *d*, which is heated over a fire grate. It is closed by the lid, *g*, which is provided with a water-seal. In this lid there is a working hole, *f*, and another aperture into which fits the porcelain tube, *e*, to lead off the fumes. Both these openings are provided with water-seals, and the porcelain tube communicates with a leaden pipe by means of a similar seal.

The bullion is charged into the dissolving pot either in the form of granulations, or of thin slabs, as at Balbach in Newark, and at San Francisco. The latter shape has, according to Gutzkow,[1] the advantage that there is but little foaming, so that the pots can be kept in continuous ebullition, and the operation is performed more rapidly than with granulations, which cause the sulphuric acid to foam up violently.

After the bullion has been charged, an amount of acid equal to twice the weight of the alloy is introduced, and the temperature is cautiously raised.

[1] *Dingl. Journ.*, vol. 225, p. 303.

In dissolving granulations, violent effervescence and a tumultuous evolution of sulphur dioxide take place, so that the acid is often added in several lots, and not all at once. If the bullion contains copper, it must be repeatedly stirred to prevent the sulphate of copper settling down and encrusting portions of the bullion. According to the size of the charge and its richness in silver, 4 to 12 hours are required for dissolving out the silver. When the solution is complete, which may be known by all hissing sound having ceased, and by no hard lumps being felt in the bottom of the pot when an iron rod is introduced into it, the

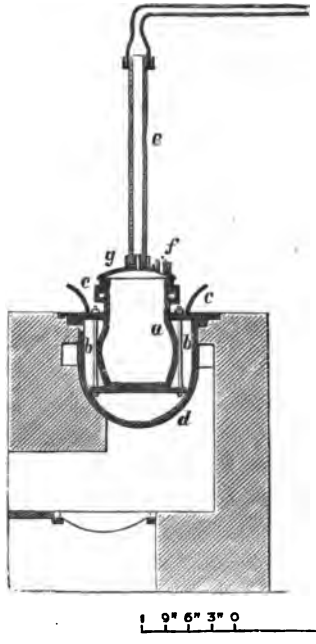


FIG. 563.

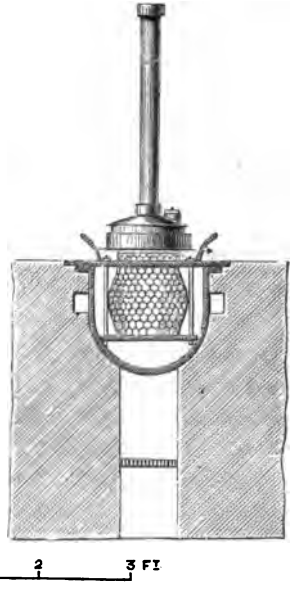


FIG. 564.

solution is in most works allowed to cool and settle. The anhydrous sulphates of copper, iron and lead are then deposited with the gold. The solution is pale green, when rich in silver, brownish, when poorer. In many cases it is white and turbid, due to sulphate of silver separating out when the solution has been cooled too far, or to suspended ferrous or lead sulphate.

The clarified and cooled fluid is, in the case of iron pots, ladled out with iron or copper ladles into a second pot or a leaden tank, or syphoned off by a leaden syphon. In some parting establishments (in France and England) the entire contents of the pot are drawn off,

without having been allowed to settle, by a platinum syphon, into a leaden vessel containing a certain quantity of water. In this vessel the mass is heated to boiling by means of steam, whereby the sulphates are dissolved, while the gold settles; the solution is then drawn off. When porcelain vessels are employed, the silver solution is poured off into leaden vessels.

The further treatment of the silver solution will be subsequently described.

The fuel consumption varies with the length of time employed in solution. For instance, at Kremnitz, in dissolving 8,000 ounces of granulations containing 10 per cent. of gold, the consumption of wood is 70 to 106 cubic feet.

3. *Treatment of the Residue for Gold*

The gold-bearing residue still retains some silver, and is therefore boiled up repeatedly (up to seven times) with concentrated sulphuric acid in dissolving vessels or smaller pots. It is then boiled with water to remove anhydrous sulphates. In many places, *e.g.* Lautenthal, it is then again treated in small cast-iron pots to remove further portions of silver. It is however impossible to get rid of all the silver by sulphuric acid; according to Pettenkofer some per cents. of silver are always retained by the gold. If gold free from silver is required, chlorine can be passed into the molten alloy as explained under parting in the dry way, or the gold may be fused with sodium or potassium bisulphate as at Freiberg, or the gold may be dissolved in aqua regia, the silver remaining behind as insoluble chloride, whilst the gold is precipitated from the solution by ferrous sulphate or chloride, as at Lautenthal or Frankfort.

Potassium and sodium bisulphate at a melting heat convert the silver in the gold into sulphate. The latter can be leached out by boiling the mass with sulphuric acid and then with water. The usual method is to mix the dry pulverulent gold with one-fourth its weight of calcined Glauber's salt, transfer the mixture to a cast-iron pot, and to add English sulphuric acid in small quantities (6 to 6½ parts of acid to 10 parts of salt). After the first portion of acid has been added, the pot is heated until its contents are fused; when no more acid fumes are evolved, a second portion of acid is added and the heating is continued for a while. Finally it is boiled up with a large quantity of sulphuric acid. By this means the gold can be brought up to a fineness of 998 per mil.

The purest gold, completely free from silver, is obtained by Roessler's method, which consists in dissolving the gold, after it has

been boiled in sulphuric acid, in aqua regia in a porcelain vessel, whilst the silver remains as chloride, and any osmiridium present is not attacked, and can be filtered off from the gold solution. The gold, precipitated from this solution by means of ferrous sulphate or chloride, is dried and melted in crucibles with borax; it is thus obtained 999·4 to 999·9 per mil. fine.

In Lautenthal 6,400 ounces of granulated gold-silver bullion are boiled in the cast-iron pots shown above (Figs. 561, 562) with 880 lbs. of sulphuric acid of 66°B. for 10 to 12 hours. The silver sulphate solution is allowed to cool, and is then ladled out. The residue is removed after every fourth boiling, so that it represents the gold from 25,600 ounces of granulations. After being boiled with concentrated sulphuric acid, it is boiled with water in a leaden tank by the aid of steam to remove the anhydrous sulphates. It is then boiled up several times with concentrated sulphuric acid in small cast-iron pots. The gold is now 920 per mil. fine. After being thoroughly washed it is dissolved in aqua regia, in a vessel of the shape shown in Fig. 565. The solution is filtered off from the precipitate, which

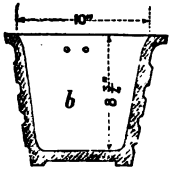


FIG. 565.

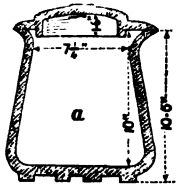


FIG. 566.

consists chiefly of chloride of silver, and is warmed on the sand-bath with ferrous chloride in a porcelain vessel of the shape shown in Fig. 566. The completion of the precipitation of the gold is indicated by a violent evolution of nitrous fumes, produced by the reaction of the excess of ferrous chloride upon the nitric acid. The precipitated gold is washed till the washings are free from iron. It is then dried in a porcelain basin and fused in a Hessian crucible with potash and meal. Three of the lumps of gold thus produced, weighing about 50 ounces each, are melted together in graphite crucibles and cast into bars. The chloride of silver is boiled up again with aqua regia and then reduced by iron and sulphuric acid. The platinoid metals will be found in the filtrate from the precipitated gold.

In Freiberg[1] 12,900 to 16,000 ounces of granulations are treated

[1] *Ann. des Mines*, 1875, vol. vii., p. 339; *Berg. und Hütt. Ztg.*, 1871, p. 247; *Freibergs Berg. u. Hüttenwesen*, 1893, p. 333.

with twice their weight of sulphuric acid in cast-iron pots for 8 to 12 hours. After cooling for 10 to 12 hours, the solution of sulphate of silver is ladled out, and a fresh charge is put in and boiled with sulphuric acid in the same way. The residues from 2 to 3 dissolvings are boiled with water in a wooden tank lined with lead, by means of steam, boiled twice with sulphuric acid in a small cast-iron pot, washed with water in a porcelain basin, and dried on a graphite slab. It is then treated in a cast-iron pot 18·5 inches high, 10·3 inches diameter at the mouth, and 0·5 inch thick, with fused sodic bisulphate in the proportions of 1 : 2, 64 ounces of gold being treated at a time for a space of 2 to 3 hours. The fused mass, which is yellowish green or brownish, is poured on to an iron slab, and after cooling is washed with hot water in porcelain vessels. The residual gold is dried on a slab of graphite, and, to remove further impurities, especially platinum, is heated slowly in quantities of 100 to 120 ounces with ½ to ⅛ per cent. of nitre in graphite pots for 5 to 6 hours, and then kept melted for another 5 to 6 hours. Gold is thus obtained free from platinum; it is remelted in graphite crucibles and poured into iron moulds. The platinum is converted by nitre into platinate of potash, which goes into the slag. The fineness of the gold is 997 to 998 per mil. The slags, obtained by melting the gold with bisulphate of soda as well as with nitre, contain platinum. They are smelted with litharge and charcoal, producing platiniferous lead, which is cupelled. The metal thus obtained is treated with aqua regia, which dissolves the platinum; the latter is recovered by precipitating with salammoniac and igniting the precipitate.

At the mint at Kremnitz, in Hungary, 8,000 ounces of granulations are boiled with twice their weight of sulphuric acid of 66°B. in cast-iron pots for 4 to 5 hours. The residue thus obtained is boiled again in the dissolving pot for 1½ hours with 123 lbs. of fresh sulphuric acid of 66°B., and then boiled up from 2 to 5 hours more, according to its purity, with sulphuric acid, in smaller cast-iron pots, 23 inches in diameter and 21½ inches deep. To each 2,250 ounces of gold 31 to 33 lbs. of sulphuric acid of 66°B. are added. The time of a boiling up is 4 to 5 hours, and the fuel consumption is half as great as it is in dissolving the granulations (see page 862).

The gold is boiled with water in stoneware vessels set on a sand bath to remove the anhydrous sulphates. It is then boiled repeatedly with dilute nitric acid, in order to remove metallic lead and an additional quantity of silver, in stoneware vessels 12 inches high and

20 inches inside diameter. The gold is then washed clean, and dried in quantities of 2,250 ounces in crucibles set in air furnaces, the heat being raised until it agglomerates so as to prevent loss in the form of dust when it is being melted.

The sintered gold is melted in charges of 1,600 to 3,200 ounces in graphite crucibles under a cover of borax, and with the addition of nitre. If the gold still contains traces of lead, cupric chloride is added to remove the latter. For fusion, the fuel consumption is 88 to 120 lbs. of coke for 1,900 ounces of gold. The fineness of the gold so obtained is 995 parts per mil.

In the United States mint at New York, the bullion charge is 300 to 400 lbs., which is boiled in cast-iron pots with sulphuric acid, added in two lots. The gold is boiled up 7 times more with sulphuric acid in pots of the same size as the dissolving pot. After the fifth and seventh acid boilings, the gold is boiled with hot water; finally it is washed upon a filter of cloth. The gold so obtained is 996 to 998 per mil fine. Coarse-grained gold is dried and melted in graphite pots; when it is fine-grained it is first pressed in a hydraulic press before drying and melting. During the fusion nitre and boneash are added to soften it.

At the works at Balbach in Newark, the bullion to be parted is cast in thin slabs. About 8,000 ounces of these slabs are charged into the cast-iron dissolving pots and dissolved in concentrated sulphuric acid. The residual gold, amounting to about 1 per cent. of the alloy, is melted with some silver and then parted by nitric acid. Alloys that contain platinum (produced from the anode mud from the electrolysis of certain kinds of copper) are treated direct with nitric acid. The platinum is thus dissolved with the silver, and after the latter has been precipitated as chloride, the former is thrown down by means of zinc.

At the San Francisco Assaying and Refining Works in San Francisco, a portion of the bullion is also dissolved in the form of slabs in cast-iron pots. Another portion is dissolved in the form of granulations. The alloy in slabs contains 2 to 10 per cent. of gold; the granulations contain 2 parts of gold to 3 of silver.

The bullion is dissolved in cast-iron pots 26 inches in diameter and 17¾ inches deep. They are provided with leaden hoods, from which a lead pipe carries the sulphurous vapours first into a little lead chamber and then into a condensing chamber filled with wet coke. The charge for a pot is about 3,200 ounces in the form of granulations, or 4,800 ounces in bars. The sulphuric acid stands 9 to 10 inches high in the pots. The dissolving takes 3 to 4 hours.

The silver sulphate solution is ladled off, and the gold, if produced from granulations, is boiled again for another 2 hours with sulphuric acid, whereas the bars are brought by the first boiling to a fineness of 996 per mil, and do not need a second boiling. The gold in either case is then washed first with acid, next with hot water, pressed, dried and melted. Its fineness is 990 to 994 per mil.

At Oker 200 ounces of granulations (containing 95 per cent. silver and ½ per cent. gold) are treated with 31 lbs. of sulphuric acid for 6 hours in a porcelain vessel. After the gold has settled for 5 hours, the silver sulphate solution is poured off into a leaden pan. The gold from several charges is boiled repeatedly with sulphuric acid in a porcelain vessel, washed, dried in a porcelain dish, and melted in quantities of 160 ounces in graphite crucibles under a borax cover. The gold is poured into waxed cast-iron moulds and is 985 parts per mil fine.

4. *Recovery of Silver from the Silver Sulphate Solution*

The silver is precipitated from the sulphate solution by means of copper, iron or ferrous sulphate.

When copper is used, the solution from the dissolving pots is transferred to tanks generally made of wood, lined with lead, in which sheets of copper are set or suspended. The solution is diluted with water and acid washings, and, to prevent the sulphate of silver from separating out in the solid state, it is heated to boiling by the introduction of live steam.

As soon as the solution no longer reacts for silver, the solution of sulphate of copper thus formed is drawn off from the precipitated silver known as *cement silver*. Theoretically, to precipitate 100 parts by weight of silver, 29 parts of copper are required, 115 parts of copper sulphate being produced; the latter is crystallised out from the solution.

When iron is employed to precipitate the silver, the sulphate of silver is first separated out in the solid form. With this object the silver solution is ladled out of the dissolving pot into another one, in which it is cooled and diluted, until the greater part of the sulphate of silver is precipitated as a greenish-white, cheesy mass. This mass is shovelled into a lead-lined wooden tank, whilst the acid solution is added in dissolving fresh lots of bullion. The sulphate of silver is packed in layers alternating with layers of sheet iron (button makers' clippings answer best), which precipitates the silver with a marked elevation of temperature. To accelerate the precipitation, the mass is stirred with wooden paddles. The iron is so proportioned

as to precipitate the silver only and not the copper. In consequence of the action of free sulphuric acid upon the iron, gases are evolved which may carry with them particles of the solution, and cause loss of silver. To overcome this objection, the precipitation is carried out in shallow wooden lead-lined trays. It is also necessary to use steam injectors or chimneys with powerful draught to protect the workmen from breathing these gases, and the particles of solution carried off by them.

The method of precipitation by iron has the advantage of economising fuel and steam for heating the solution and of employing a cheaper precipitant.

When the silver is precipitated by ferrous sulphate (Gutzkow's method), the sulphate of silver is also obtained in a solid (crystalline) form by cooling and diluting the solution. The crystals of sulphate of silver thus separated are thrown on to a filter, and a hot solution of ferrous sulphate is run on to them. Metallic silver is reduced, ferric sulphate being formed and going into solution, thus :—

$$Ag_2SO_4 + 2FeSO_4 = Ag_2 + Fe_2S_3O_{12}.$$

The ferric sulphate solution is collected in a leaden tank standing below the filter. If the sulphate of silver contains copper, a copper-bearing solution runs off first, which is collected separately and the copper precipitated by means of iron. The ferric sulphate solution is converted into ferrous sulphate (which is used to precipitate fresh quantities of silver sulphate) by the introduction of iron.

Cement silver, produced by any of the above methods, is first freed by sieving from any lumps of copper it may contain, and is then washed with water on filters or in wooden tubs, until the washings no longer react for copper, iron or sulphuric acid. The silver is then freed from the greater portion of its water by being squeezed in linen, or in screw or hydraulic presses, the last-named being preferable. The cakes of silver, so obtained, are heated on iron plates or in round or oval cast-iron pipes, broken up, melted in clay or graphite crucibles and cast into bars. In order to remove any foreign substances, nitre is added, and the slag formed is skimmed before the silver is poured. The moulds, into which the silver is poured, are coated with clay or lime, and are covered up as soon as the silver has been poured in. The silver thus obtained is 998–999 parts per mil fine.

The solutions left after the precipitation are worked up for blue-stone or green vitriol as the case may be.

The washings are used to dilute the solutions for the precipitation of silver.

The dross produced in melting the silver and also the gold is smelted with potash or litharge, or added during the cupellation of work-lead.

The old crucibles are broken up and added during the smelting of silver ores, or else they are treated with dilute sulphuric acid and amalgamated.

In Freiberg the silver sulphate solution, after being allowed to cool for 10 or 12 hours in the dissolving pot, is ladled with copper ladles into copper vessels and from these into wooden tanks lined with hard lead (5 feet 2 inches long, 4 feet 2 inches broad, and 3 feet 4 inches deep). In these the silver is precipitated by means of sheet copper, the solution being heated by steam to 70° C. The silver is pressed through a sieve which retains all pieces of copper, washed with hot water in a wooden vat furnished with a false bottom and a linen filter, pressed in a hydraulic press into cakes 30¾ inches in diameter, dried strongly in iron retorts 3 feet 4 inches long and 9¼ inches in diameter, melted in black lead crucibles 37 inches high, and 18½ inches wide at the mouth, and finally cast into bars of 960 ounces in weight, or granulated. The silver is 998 to 999 per mil fine.

The practice in Kremnitz is similar. The precipitating boxes are 8 feet 2 inches long, 4 feet 3 inches broad and 2 feet 8 inches high. The silver sulphate solution is diluted to 24° B. before the silver is precipitated. The cement silver is washed with hot water in a filter supported by a perforated copper funnel; it is pressed into cakes by a hydraulic press, heated in oval cast-iron retorts, melted in charges of 16,000 to 19,000 ounces in graphite crucibles, and finally cast into moulds. The fuel consumption in the air furnace for the above charge is 220 to 310 lbs. of coke.

The solution of sulphate of copper obtained by precipitating the silver is evaporated down to 44° B., and then allowed to crystallise. The bluestone crystallises upon twigs of birch; the coarse bluestone thus produced is dissolved in water, the solution (at 37° to 38° B.) again evaporated, and allowed to crystallise. The crystallising pans are heated by steam.

In the New York mint the silver is also precipitated by means of copper. The precipitating tanks are 7 feet long, 5 feet wide, and 3 feet 10 inches deep. The copper, in the form of slabs, is stood round the sides, and laid on the bottom of the tank. The silver sulphate solution is diluted with wash water to 20° B., and boiled with live steam for 6 or 7 hours. The precipitated silver is filtered on a linen filter supported by a copper vessel, washed in a leaden tank with hot water, pressed in a hydraulic press, dried by live steam for 18 hours

in a copper steam drier, and melted in graphite crucibles in charges of 4,500 to 6,000 ounces with nitre and boneash. The silver, cast into bars, is 990 to 998 per mil fine.

The copper sulphate solution is concentrated to 35 to 40° B., and allowed to crystallise, the crystals forming on strips of lead.

The precipitation of silver by iron is carried on, *e.g.* at Lautenthal in the Upper Harz. The cooled solution of sulphate of silver is ladled by means of copper ladles into a cast-iron pot standing beside the dissolving pot, and there diluted with cold water down to 58° B., by which means the sulphate of silver is separated as a greenish-white cheese-like mass. The latter is transferred to a lead-lined wooden tank for the reduction of the silver, whilst the solution is added when

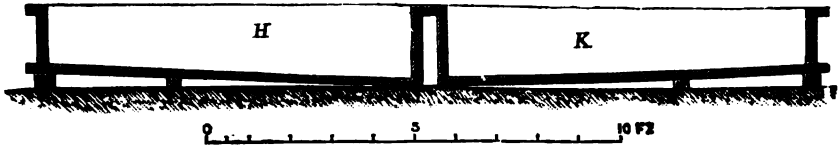


Fig. 567.

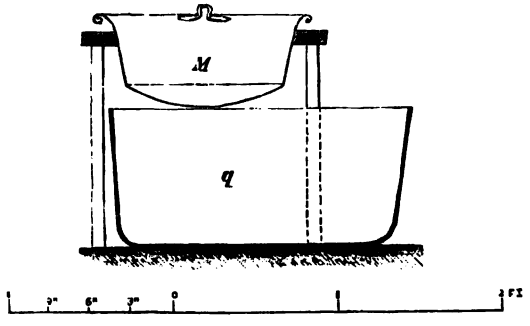


Fig. 568.

fresh lots of bullion are being dissolved. The precipitating tank, together with the tank standing beside it to receive the washings from the silver sulphate, are shown in Fig. 567. *H* is the precipitating tank, *K* the tank for the washings. Both have inclined bottoms, are constructed of wood, and lead-lined. The sulphate of silver is placed in layers with button-makers' clippings, which are added gradually, and very cautiously towards the end of the precipitation. The washings contained in the tank *K* are added, and the mass stirred with wooden shovels during the precipitation. The precipitation is complete when salt ceases to produce any turbidity in the solution; it lasts 2 to 3 hours. The precipitated silver is transferred to a filter of linen supported in a vessel made of perforated sheet copper of the

shape shown in Fig. 568, and washed with hot water till ferrocyanide of potassium no longer gives an iron reaction with the washings. The latter are, as already stated, collected in the tank *K*, and added during the precipitation of the silver. The cement silver is pressed in a hydraulic press, heated in a cylindrical cast-iron retort, melted with nitre in quantities of 6,400 to 8,000 ounces in graphite crucibles, and poured into cast-iron moulds.

The solution of ferrous sulphate is filtered through a filter of

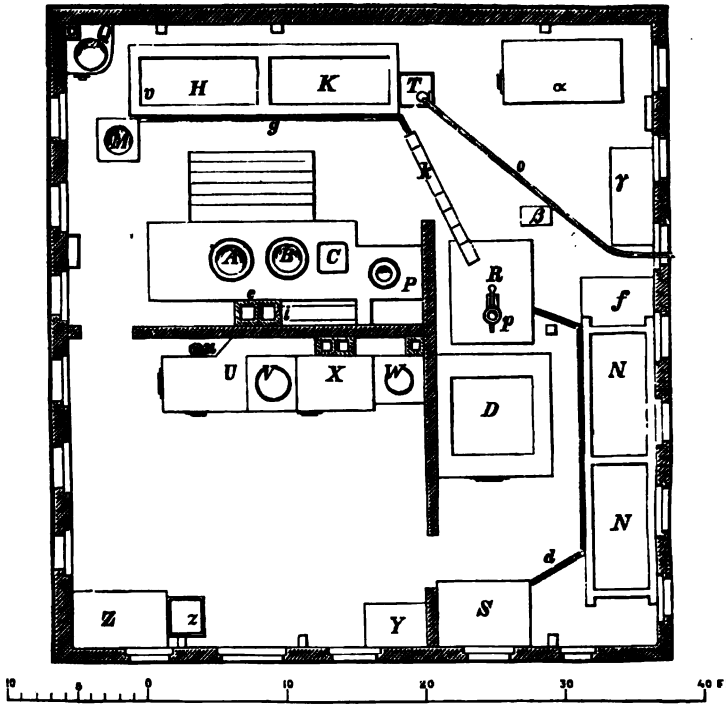


FIG. 569.

granulated lead, evaporated in basins with the addition of iron, and allowed to crystallise in tanks.

The ground plan of the Lautenthal parting works is shown in Fig. 569. *A* is the dissolving pot, *B* the pot for receiving the solution of silver sulphate, *C* a leaden tank into which the acid is ladled from *B*, from off the solid sulphate of silver, to be subsequently used in preparing further solutions, *e* the stack for carrying off the sulphurous vapours, *H* the precipitating tank, *K* the tank for washings, *M* the filter on which the cement silver is washed, *Q* a boiler for hot water,

R a receiver for the iron-bearing solutions, *Y* the hydraulic press, *v* the retort for heating the pressed silver, *V* the air furnace for melting silver, *W* for melting gold, *k* a trough with a filter of granulated lead through which the solutions containing iron are run, *p* an injector to convey the solutions of ferrous sulphate to the evaporating pans *D*. *N*, *N* are crystallising tanks for the ferrous sulphate. *T* is a leaden tank for freeing the gold from sulphates by boiling with water, *o* being the steam pipe by which the latter is heated, *P* is a pot for boiling the gold with sulphuric acid, *a* a sand-bath, *γ* a work bench, *S* a lead lined tank for collecting crystallised green vitriol.

Gutzkow's method of precipitating the silver from the solution of sulphate by means of ferrous sulphate was in use at the San Francisco Assaying and Refining Works; these works are no longer in existence. According to Egleston[1] the process was carried out as follows:—

The silver sulphate solution was drawn off from the dissolving pot into an iron tank 9 feet long, 5 feet wide, and 20 inches deep, containing sulphuric acid at 58° B. (being the mother liquor drained from precipitated silver sulphate), and was then heated by external firing to 110° C. The dilution caused the precipitation of sulphate of lead, which carried down any suspended particles of gold, whilst the high temperature kept the sulphate of silver in solution. The clear solution was drawn off into a second iron tank, standing in a leaden one, and cooled by the circulation of cold water in the space between the two, whereby the sulphate of silver was precipitated, forming a hard yellow crystalline incrustation on the bottom of the tank, this process taking 9 hours. At the end of this time the supernatant mother liquor was forced back into the first iron tank, where it forms the acid at 58° B. used for diluting sulphate of silver solution.

The sulphate of silver, which contains intermixed cuprous oxide as a red powder, was transferred to wooden boxes lined with lead and provided with false bottoms, 4 feet long, 35 inches wide, and 12 inches deep. One such box received the silver sulphate from 5 dissolving pots. Hot concentrated solution of ferrous sulphate as neutral as possible was then run in; it penetrated through the layer of silver sulphate, reducing it to metal and becoming converted to ferric sulphate, and, passing through the false bottom, ran off by a stopcock close to the true bottom of the tank. The solution that escaped first, contained the copper, and was therefore blue; it was run into a special lead-lined tank. As soon as the solution was free from copper, as indicated by its brown colour, it was run into a tank lined

[1] *Op. cit.*, p. 775.

with lead, 18 feet 4 inches long, 9 feet 2 inches wide and 3 feet deep. As soon as the colour of the escaping solution changed to green the greater part of the silver sulphate had been reduced, and the

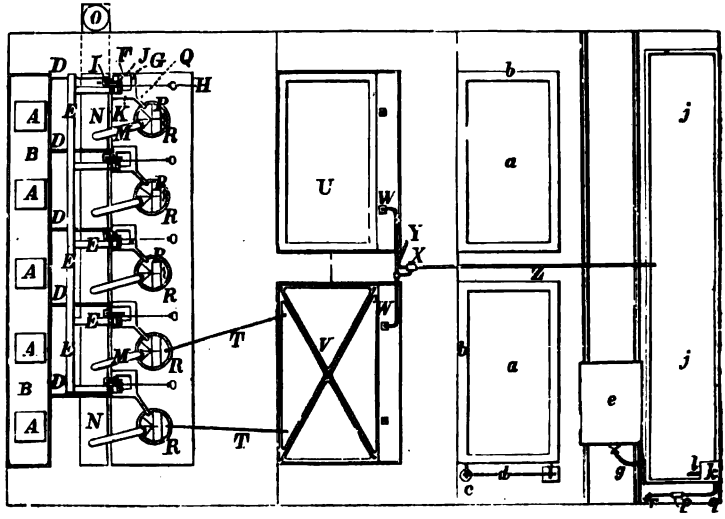


FIG. 570.

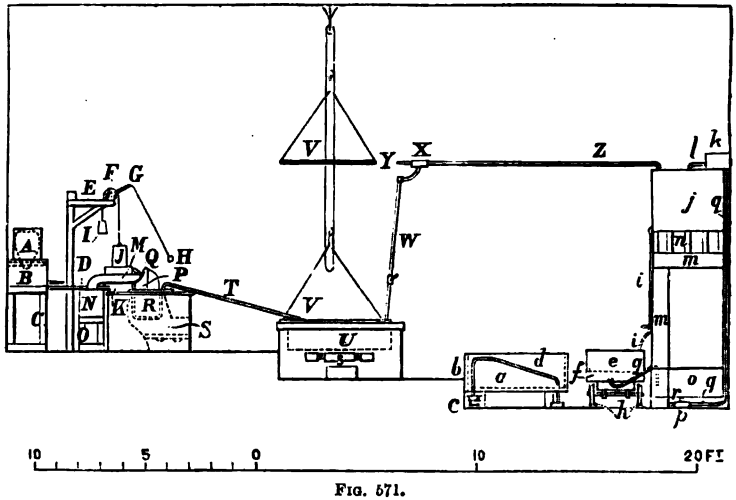


FIG. 571.

supply of ferrous sulphate solution was stopped. The entire process lasted 4 to 5 hours, and the mass had to be stirred from time to time in order to expose fresh surfaces of the silver sulphate to the ferrous sulphate solution. The quantity of this latter used was 7·9 gallons

to 100 ounces of silver. The solutions escaping contained a small amount of silver sulphate, about 7½ per cent. on the average. The silver was precipitated from them in the above-mentioned tanks, by means of copper from the blue solution and by means of iron from the brown.

The precipitated silver amounted to 90 per cent. of the total silver present, but it still retained a small quantity of sulphate of silver. To reduce the latter, the silver was transferred to a tank lined with lead, 4 feet long, 3 feet wide, and 3 feet deep, provided with a false bottom and a filter; it was arranged in layers 10 inches deep, between which were copper plates, and allowed to stand in hot water over night. The hot water dissolved the sulphate of silver which was reduced by the copper.

The silver was then washed with hot water on a filter of linen, dried, pressed in a hydraulic press, ignited and melted in blacklead crucibles; it was 998 per mil fine.

The ferric sulphate solution was again reduced to ferrous sulphate, which was used to precipitate fresh quantities of silver sulphate, by being boiled with scrap iron.

The arrangement of these works is shown in Figs. 570 and 571.[1] *R* are the dissolving pots; *M* the draught pipes for removing the sulphurous vapours; *N* small lead chambers, communicating with a coke tower *O*; *B* are sulphuric acid tanks; *U* tanks to receive the silver sulphate solution; *a* are tanks in which the sulphate of silver is crystallised; *e* is a tank on wheels for precipitating the silver; *j* is the tank for the solution of ferrous sulphate; *o* the tank in which the ferric sulphate is reduced to the ferrous state. The latter solution is drawn by the steam-pump *p* into the tank *K*, and flows from the latter into the reservoir *j*.

C. Parting of Gold by the Electrolytic Method

When auriferous gold is used as the anode, a plate of silver as the cathode of an electric current, and a highly dilute solution of silver nitrate as the electrolyte, the silver can be thrown down at the cathode, whilst the gold remains in a pulverulent form at the anode, provided that a current of suitable strength is used.

By enveloping the anode in a cotton bag the gold can be collected in the latter. The solution of the anode takes a comparatively short time. The silver so obtained is free from gold, whilst the gold can be freed by boiling with nitric acid from the small quantity of silver

[1] Egleston, *op. cit.*, p. 776.

which it still contains, and can be brought to a fineness of over 999 per mil.

If the bullion is impure, it must first be refined before electrolysis, and brought to a fineness of at least 950 per mil. A large proportion of copper should be more particularly avoided, because it is precipitated with the silver at the cathode.

Electrolytic parting of gold and silver, which depends on the principles above enunciated, has been introduced by Moebius in Pittsburg and St. Louis, and a few years ago in the parting establishment at Frankfort-on-the-Maine, and has shown itself capable not only of holding its own, but of displacing at these works the method of parting by sulphuric acid.

It can be used on silver containing 0·2 of gold per mil; and, apart from its greater cheapness, has the advantage, compared with refining, that no injurious vapours are evolved. The parting is moreover complete in 48 hours, and the losses of silver are less. It may therefore be expected that it will replace refining by sulphuric acid in other large works.

At St. Louis, where the author saw the electrolytic method in operation at the works of the St. Louis Smelting and Refining Company, which commenced operations in 1891, the silver to be parted contains five parts of gold per mil. It is cast into anode plates 10 inches long, 8 inches wide and ¼ inch thick; these plates are suspended, coupled together in pairs, to form an anode in the baths. The cathode plates consist of thin rolled sheets of pure silver. The electrodes are suspended in ten boxes, made of pitch pine and rendered watertight with ozokerite. Each of these boxes has seven divisions, so that there are formed seventy baths with four pairs of electrodes in each. The difference of potential in the bath is 1½ volts, and the current density is 33 ampères to the square foot. The current is furnished by a dynamo with a strength of 200 ampères and a tension of 100 volts, manufactured by the United States Electric Light Company, and consumes 15 H.P. The entire works are supplied by a 30 H.P. Westinghouse engine.

The anode plates are enveloped in linen sacks.

The silver does not separate out in the compact form but in crystals, so that short-circuiting readily occurs. A scraping arrangement is therefore used, running on rollers along the cover, which destroys any short circuits, and at the same time keeps the solution in movement. The silver falls into a wooden box set under the electrodes of each bath, and provided with a false bottom and a filter. The false bottom is perforated and covered with linen, so that the

silver is retained on it. By a simple arrangement this box can be lifted out of the bath when desired.

At the commencement of operations the electrolyte consists of water with $\frac{1}{10}$ per cent. of nitric acid, and subsequently of a very dilute solution of silver nitrate.

The anode plates are consumed in 36 to 40 hours. The gold collects in the bags, the silver in the filter boxes. The former is removed once a week, the latter every evening, by lifting the boxes out and emptying them one after another into a box provided with a sieve, which is pushed along from bath to bath.

The gold mud still contains silver and is therefore boiled with nitric acid, washed, dried, and melted with sand or borax. The gold so obtained is 999 per mil fine. The nitrate of silver thus produced and the washings of the gold are added to the electrolyte in the bath.

The crystals of silver are washed in the box in which they are collected, which is also furnished with a filter, then dried by means of air drawn through it and melted. The silver is 999·5 per mil fine, and is free from gold.

With the above installation, 30,000 ounces of auriferous silver are parted every 24 hours.

The silver treated at Pittsburg, where the method has been in operation since 1887, also contains 5 parts of gold per mil. It is cast in closed moulds into plates 10 inches wide, 16 inches long, and $1\frac{1}{4}$ inches thick. The arrangement is similar to that at St. Louis. The anodes are consumed in 48 hours.

The gold mud is melted with some silver and boiled with nitric acid in stoneware pots; 40,000 ounces can be parted in 24 hours with a consumption of 20 H.-P. Natural gas is used for firing.

The works of the German Gold and Silver Parting Establishment at Frankfort-on-the-Maine is, according to Dr. Roessler, intended for parting 32,000 ounces of *blicksilver* per 24 hours. The dynamo (on the Schuckert system) requires 20 H.P., and is driven by a 25 H.P. gas engine. It gives a current of 150 ampères, with a tension of 100 volts; 70 cells are in use, each of which absorbs $1\frac{1}{2}$ volts.

The anode plates are rectangular, are 0·4 inch thick, and weigh each 48 ounces. These plates, in sets of four contained in linen bags, are suspended opposite each cathode, which is made of rolled sheet silver.

The electrolyte is a feebly acid solution of copper nitrate containing 0·4 lb. of copper and 0·05 lb. silver to the gallon. In 36 hours the anodes are consumed, all except the portions projecting

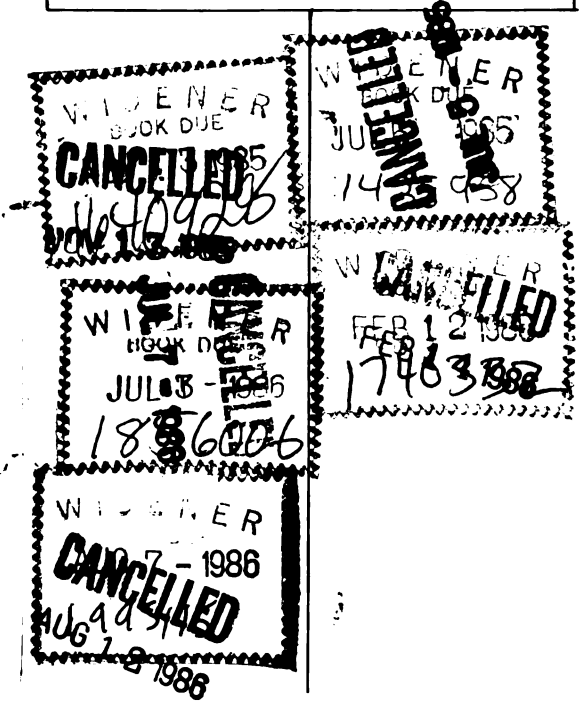
from the solution. When the silver is rich in gold and copper, the tension required is markedly higher than in the case of silver with but little gold and copper.

The silver is removed every 24 hours, the gold every 72 hours, from the baths. The silver is in small sparkling crystals, and can be melted direct, being then 999 per mil fine.

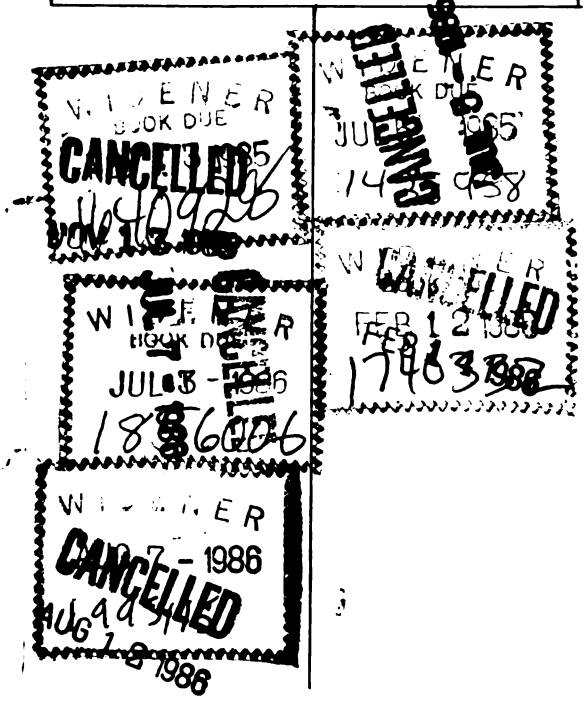
The gold still contains silver, peroxides of silver and of lead, and various other impurities; it has accordingly to be refined.

Quite recently attempts have been made at Hamburg, St. Petersburg, etc., to electro-deposit pure gold, a solution of gold chloride being used as the electrolyte and the silver present being thrown down as chloride in the anode-mud; platinoid metals are said to pass partly into solution, and partly to be deposited in the anode-mud. The method is technically quite feasible, but nothing is known of the economic results obtained.

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